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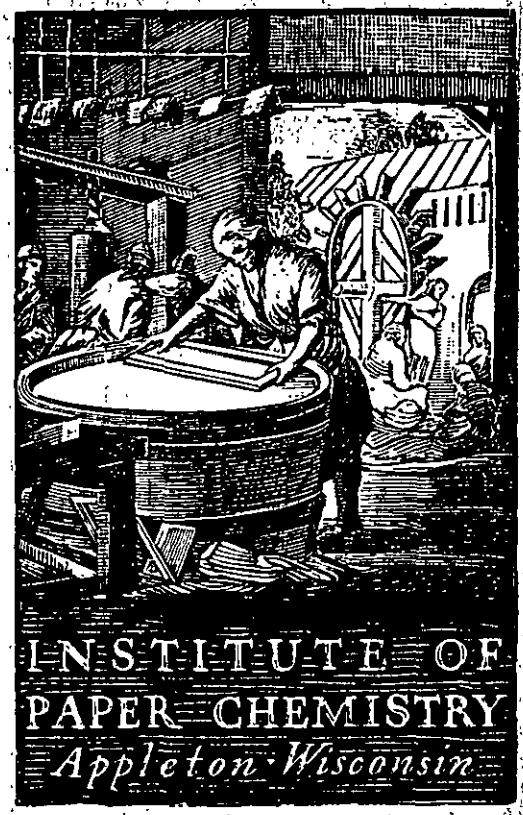

SELECTIVE DELIGNIFICATION OF WOOD AND OTHER FIBROUS MATERIALS

ANALYSIS OF HOLOPULPING PROCESSES

Research Grant

Project 2500

Report Eleven

A Progress Report

to

THE GRANTORS

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SELECTIVE DELIGNIFICATION OF WOOD AND OTHER FIBROUS MATERIALS

ANALYSIS OF HOLOPULPING PROCESSES

SUMMARY

An evaluation of the holopulping process has been made. A complete system incorporating chemical recovery appears to be technically feasible. The process incorporates electrolytic production of chlorine and caustic and sodium chlorate and is predicated on the availability of cheap electrical power. An economic analysis indicates that holopulp can be produced on a commercial scale at a cost comparable with bleached kraft pulp. It is estimated that the capital requirements would run about $25 million for 500 t.p.d. of pulp production. The cost for holopulp from aspen would run about $80 per airdry ton.

The analysis identified the areas of greatest uncertainty as a means for focusing future work. The biggest single question is concerned with evaporation and combustion of the spent liquor. Combustion products and degree of recovery must be determined and the potential for air and stream pollution identified. The next major problem is concerned with the water balance over the pulping step. This requires information on the effects of the recycling liquors, dewatering capabilities, consideration of high-consistency reactors, and the use of high-consistency washing methods. A third important factor is the possibility of using a ClO_2-Cl_2 gas mixture for the oxidation step. If this approach can be used, several simplifications in the process can be obtained. Other problem areas have also been identified.

There appears to be reason for optimism concerning the eventual commercial success of the process. If the problem areas mentioned above can be

successfully handled, there would appear to be no major technical obstacles to success. In that event, the stage would be set for serious consideration of a holopulp pilot plant.

C O N F I D E N T I A L

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SELECTIVE DELIGNIFICATION OF WOOD AND OTHER FIBROUS MATERIALS

ANALYSIS OF HOLOPULPING PROCESSES

INTRODUCTION

It has long been recognized that conventional chemical pulping processes remove a substantial amount of carbohydrate material along with lignin. Thus, pulp yield can be increased significantly if the lignin is selectively removed from the wood. Certain oxidants, such as chlorine dioxide or peracetic acid, permit selective delignification and have long been used for this purpose in the laboratory. However, pulping processes using selective delignification have never met with commercial success. This is due, in a large measure, to the high cost of the chemicals involved.

A basic objective of Project 2500 has been to investigate the feasibility of a commercial process for producing pulp by oxidative delignification. Pulps produced by such a method have been given the name holopulp. Over a period of years of work on this project, the amount of chemical required has been brought down and the factors controlling the properties of the resulting product have been defined. The culmination of this work was the delineation of a sequence of operations which leads to a holopulp having desirable papermaking properties. The chemical requirements and process conditions appear to be well within the range of commercial interest. Accordingly, it is now appropriate to give serious consideration to the development of a commercial holopulping process.

A rather detailed analysis of potential holopulping processes has been carried out, and the results are presented in this report. This analysis considers the feasibility of combining a chemical recovery system with the pulping process

itself, provides for estimates of capital and operating costs and defines the technical problem areas within the process. It thus provides a basis for the assessment of commercial possibilities and defines the critical areas of the process where additional work can most productively be spent.

GENERAL DISCUSSION OF HOLOPULPING PROCESS

The complete holopulping process consists of two major parts--the pulping process itself and the chemical recovery system. Each of these parts must be completely compatible and integrable with the other. Each, in turn, introduces constraints on the other. For example, the need for chemical recovery requires that the pulping process be carried out in such a fashion that the resulting spent liquor is not too dilute. On the other hand, the chemical recovery system should have sufficient flexibility to meet the chemical demands of the pulping process. The ability to solve the problems associated with the integration of a recovery system with the pulping process will have a large bearing on the ultimate commercial success of the process.

Pulping Process

As it is presently conceived, there are four major elements to the pulping process. These are as follows.

1. Fiberization of wood chips to give fiber bundles. Fiberization is carried out before chemical treatment, using water impregnation, steaming, and mechanical refiners.
2. Oxidation of the fiberized wood with chlorine dioxide (ClO_2). This can be carried out using either ClO_2 gas or an aqueous solution of ClO_2. The reaction is carried out at atmospheric pressure and at temperatures on the order of 50°C.

3. Extraction of the oxidized material with a caustic solution. The extraction is carried out at atmospheric pressure and at temperatures less than 80°C. Most of the solubilization of material takes place during the extraction.

4. Treatment of the extracted material with a hypochlorite solution. This is also carried out at atmospheric pressure and low temperature. The hypochlorite treatment has a significant whitening action, and also aids in fiber liberation.

There are many ramifications to this pulping process. Oxidation and extraction steps could be multistaged, as, for example, in the sequence fiberization-oxidation-extraction-oxidation-extraction-hypochlorite. An alkaline pretreatment (essentially an extraction) could be carried out before any oxidations. It is conceivable that alkaline extraction could be carried out simultaneously with the fiberization step. The hypochlorite step could be dropped for certain grades or the hypochlorite and oxidation steps could possibly be interchanged. Another variation on this same basic process would be the use of varying amounts of chlorine along with the ClO_2 in the oxidation step.

Despite all the variations mentioned above, the basic elements of the pulping process are fiberization, oxidation, extraction, and hypochlorite treatment. For the purpose of this process analysis, the basic sequence of fiberization-oxidation-extraction-hypochlorite is used with the provision that the oxidation is generalized to include chlorine as well as chlorine dioxide as the oxidants. The reason for this latter provision will become evident during the discussion of the chemical recovery system.

Regardless of the sequence used in pulping, the chemicals which are used are chlorine dioxide (ClO_2), chlorine (Cl_2), caustic (NaOH), and hypochlorite (NaOCl). Since hypochlorite can be formed by the reaction

$$Cl_2 + 2NaOH \rightarrow NaOCl + NaCl + H_2O$$

as needed, the basic chemicals required for this pulping process are ClO_2, Cl_2, and NaOH.

Chemical Recovery System

Ideally, a chemical recovery system will treat the spent liquor from the pulping process so as to provide the chemicals needed for pulping. In the case of the holopulping process described above, the chemical recovery system must supply ClO_2, Cl_2, and NaOH. Hence it is necessary to recover the sodium and the chlorine from the spent liquor and process these to produce ClO_2, Cl_2, and NaOH. This must be done in such a manner that volatile chlorine compounds are not released to the atmosphere since these would constitute an air pollution problem.

The chemical recovery system can be broken into three areas as follows:

1. Collection, concentration, and burning of spent liquor.
2. Production of chlorine and caustic.
3. Production of chlorine dioxide.

The process of collecting, concentrating, and burning the spent liquor could follow conventional chemical recovery practice. Pulp washing would be carried out in as efficient a manner as possible to provide maximum recovery of sodium and chlorine with a minimum of dilution. Concentration of the weak spent liquor to the degree required for combustion would be carried out in multiple effect evaporators. The concentrated liquor could then be burned in a furnace to allow

recovery of the inorganic chemicals as a mixture of NaCl and Na_2CO_3 (salt and soda), dependent on the relative abundance of Na and Cl in the liquor. The heat from combustion could be used to generate steam.

In order to generate Cl_2 and NaOH from the salt and soda, it would be necessary to convert the carbonate to chloride. This can be done by the addition of hydrochloric acid (HCl) to the recovered material according to the reaction

$$2HCl + Na_2CO_3 \rightarrow 2NaCl + H_2O + CO_2\uparrow \ .$$

The resultant brine would then be electrolyzed to give H_2, Cl_2, and NaOH. A portion of the Cl_2 could be reacted with the necessary amount of H_2 to form the HCl needed to convert the soda to salt. A portion of the Cl_2 could be reacted with some of the NaOH to produce the necessary hypochlorite. The remaining NaOH would be available for the extraction step, while the remaining chlorine would be available for the production of ClO_2.

Chlorine dioxide can be produced from chlorine and electrical energy by a modified Day-Kesting process. The overall equation for this reaction is

$$\tfrac{1}{2}Cl_2 + 2H_2O + (6 \text{ faradays}) \rightarrow ClO_2 + 2H_2 \ .$$

A recent version of this process patented by Chemech Engineering Ltd. appears to be especially suitable to holopulping. The Chemech process involves electrolytic production of sodium chlorate, reaction of the hydrogen produced during electrolysis with chlorine to form HCl, and reaction of the HCl with the chlorate to form chlorine dioxide. The chemical reactions for these major steps are:

$$NaCl + 3H_2O + (6 \text{ faradays}) \rightarrow NaClO_3 + 3H_2$$

$$H_2 + Cl_2 \rightarrow 2HCl$$

$$NaClO_3 + 2HCl \rightarrow NaCl + ClO_2 + \tfrac{1}{2}Cl_2 + H_2O \ ,$$

with the overall reaction given above. The complete ClO_2 generation process is self contained and produces ClO_2 from Cl_2 without liquid effluent to be disposed of.

It can thus be seen that a chemical recovery system compatible with the pulping process is conceivable. Such a recovery system is keyed to the electrolytic regeneration of the cooking chemicals, is sulfur free, and has the potential of operating without any undesirable effluent streams.

DETAILED DISCUSSION OF MAJOR PROCESS ELEMENTS

The preceding discussion has covered the essentials of holopulping and has outlined in broad terms the nature of the process. A complete holopulping process involves four major, interconnected systems. These are pulping, spent liquor processing, chlorine and caustic production, and chlorine dioxide production. In order to provide a basis for an assessment of the commercial feasibility of this process, it is necessary to consider the elements making up the process in detail.

PULPING SYSTEM

As has been mentioned previously, the pulping system may be considered as being made up of four essential components: fiberization, oxidation, extraction, and hypochlorite treatment. Each of these steps will be discussed in detail. In addition, since the pulping process consists of a sequence of distinct operations, the effect of intermediate washing on the pulping behavior must be examined. Finally, the various combinations possible with these basic process elements should also be considered.

Fiberization

The objective of the fiberization step is to subdivide the wood to provide for more uniform treatment in the subsequent chemical processing. This is a key step in the pulping process since it affects all of the operations which follow. The introduction of this fiberization step has made it possible to carry out delignification at reasonable levels of oxidant consumption. Its importance to the overall process cannot be over emphasized.

Ideally, the fiberization step would provide individual fibers separated in the middle lamella region without significant mechanical damage, hydrolytic degradation, or lignin condensation. In actual fact, this ideal cannot be attained

and the fiberized product consists of fiber bundles along with a certain amount of debris. The individual fibers are damaged or degraded to some extent. Fiberization is critical to the subsequent chemical processing, but it is difficult to characterize or describe in a quantitative manner. If the fiberization step is overdone, a significant degradation in pulp properties can result. On the other hand, if the fiberization is incomplete, subsequent chemical processing will not be as efficient. This could result in a less useful pulp and/or in excessive use of chemical. A concerted attack on the fiberization problem is currently in progress.

As presently conceived, there are three basic parts to the fiberization step. These are:

1. Impregnation of chips with water.

2. Steaming, to raise the temperature of the chips up to the point of lignin plasticization.

3. Mechanical refining to achieve fiberization.

Impregnation proceeds by deaerating the chips by steam purging, and then soaking the chips in water under pressure. This could be carried out on a commercial scale either batchwise or continuously. It is very similar to the Va-purge process. The final steaming and refining could be carried out continuously on a commercial scale using modern pressurized refiners, with an attached presteaming chamber. Hence, the fiberization step could be carried out on a commercial scale using existing technology.

Steam and electrical energy are required in the fiberization. The steam requirement will include that used to fill the void space between the chips as well as the steam used in raising the temperature of the wood. The amount of steam needed will depend on the number of purge cycles used, as well as the desired wood

temperature entering the refiner. Preliminary estimates indicate that steam requirements may amount to as much as 400 lb. PTP for two purge cycles and 200 lb. PTP for the final steaming, assuming a void fraction of 50%. A definitive value of the electrical power required is not presently available. It is presently estimated to be about 5 horsepower-days per ton of wood, which would amount to about 135 kw.-hr. PTP. It is likely that a final answer to the refiner power requirement must await pilot-scale work, so that refiner power input can be balanced against the effects on the subsequent pulping operation.

Oxidation

The primary oxidant which is used is chlorine dioxide. In addition, some chlorine is always present to a greater or lesser degree either deliberately or inadvertently. Since both ClO_2 and Cl_2 are gases which are soluble in water, the oxidation can be carried out with either gaseous ClO_2 (and Cl_2) or with an aqueous solution. Both of these methods have been demonstrated in the laboratory. It appears that the basic reaction mechanism is essentially the same in each case. The shredded wood must be moist for reaction with gaseous ClO_2 to occur. This is a strong indication that the actual reacting species exist in aqueous solution. The reaction with gaseous ClO_2 apparently occurs by the dissolution of the gas in the moisture which is present with the wood, and then reaction of this solution with the wood substances. Further evidence for the similar nature of the reactions is that the chemical requirements to obtain a given degree of delignification are essentially the same in each case.

Aqueous Oxidation

Carrying out the oxidation with an aqueous solution of ClO_2 is quite similar in operation to bleaching with ClO_2. The major difference lies in the

much greater amounts of ClO_2 which react, and the consequent reduction in consistency in the reactor. Present indications are that the amount of ClO_2 needed for essentially complete delignification is about 9% by weight on the original wood if the oxidation is carried out in a single step. If the oxidation is split into two steps with an intermediate alkaline extraction, the ClO_2 requirement is reduced to about 7.5% by weight of the original wood (5% on the first stage and 2.5% on the second stage). These consumption figures were obtained for aspen and red maple. Chemical consumption would undoubtedly be somewhat species dependent, particularly between hardwoods and softwoods.

Chlorine dioxide has only a limited solubility in water, and this introduces a severe dilution problem if aqueous-phase oxidations are used. The maximum solubility of ClO_2 in water under normal conditions (absorbing ClO_2 into water) is about 1 lb. of ClO_2 per 100 lb. of water. Assuming a single-stage oxidation requiring 9% ClO_2 on the wood, the maximum consistency in the reactor would be:

$$\frac{1 \text{ lb. wood} \times 0.09 \text{ lb. } ClO_2/\text{lb. wood} \times 100 \text{ lb. water/lb. } ClO_2}{1 \text{ lb. wood}} = \frac{9 \text{ lb. } H_2O}{\text{lb. wood}}$$

or a consistency of 10%. Actual operating consistencies would be lower than this because of the water carried in with the wood. The problem is not really one of consistency but rather one of the concentrations of spent liquors which would be obtained. Using a pulp yield of 65% as a typical value, 1 lb. of wood would give 0.35 lb. of soluble organic material. Thus, the maximum concentration of organic in the spent liquor if only the water needed to dissolve the ClO_2 is introduced (no additional water in extraction, hypochlorite, or washing) is

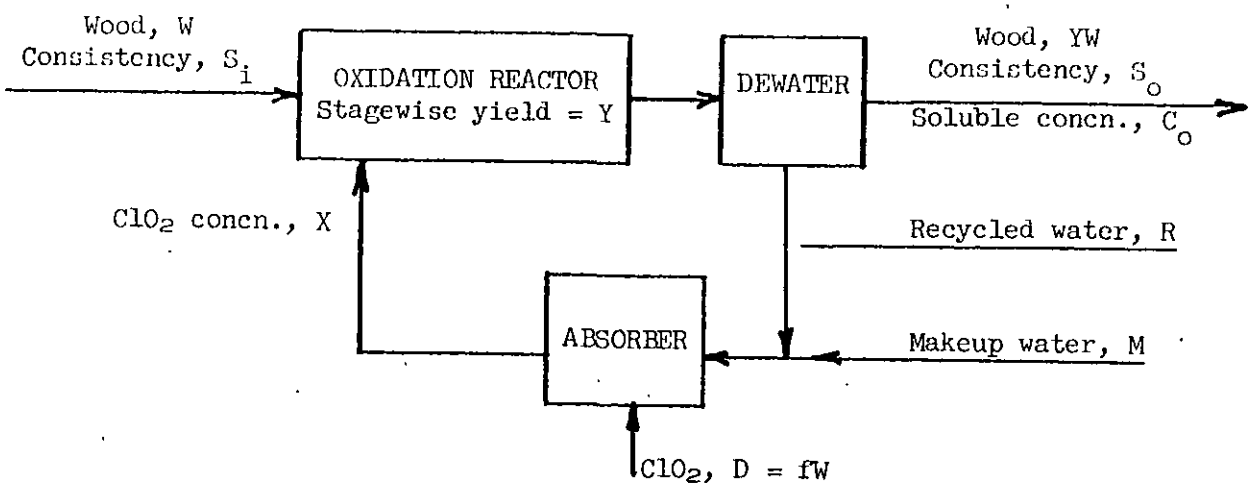
$$0.35 \text{ lb. organic}/9 \text{ lb. water} = 0.039 \text{ lb. organic/lb. water}$$

or about 3.75%. Thus, the straightforward application of aqueous ClO_2 solutions

for the oxidation step would lead to spent liquors too dilute for practical chemical recovery.

This dilution problem can be minimized by recycling the liquor around the oxidization reactor. The low-consistency material leaving the oxidizer can be dewatered to a much higher consistency. The water removed at this stage would then be sent back to the absorption tower for refortification with ClO_2 and thence back to the oxidizing reactor. The only water which would have to be added (and which would dilute the final spent liquor) would be a small make-up stream equal to the difference between the amount of water entering and leaving the stage with the wood. However, the concentration of dissolved organic material in the liquor will increase with the amount of recycle, and the total of recycle plus make-up water is fixed by the ClO_2 requirement and the solubility of ClO_2. Hence, as recycle is increased, the possibility of ClO_2 consumption by undesired side reactions is increased. This could have a pronounced effect on the efficiency of the oxidation. This problem may not be as severe as it appears since the bulk of the material is not solubilized until the alkaline extraction. A schematic diagram of this recycling method is given in Fig. 1.

Material balance equations for recycling around the oxidation reactor are included in Fig. 1. These can be used to examine the effect of recycling liquor on the build-up of organic in the liquor. In a typical case, the wood might enter at 50% consistency from the fiberization step. If the ClO_2 requirement is taken to be 9% at a solubility of 0.01 lb. ClO_2/lb. H_2O, and a stagewise yield of 96% is assumed, the amount of recycled liquor and the organic concentration will depend on the consistency after dewatering. If, for example, the exit consistency is taken to be 25%, the recycle will amount to 7.12 lb. H_2O/lb. wood, the make-up water rate would be 1.88 lb. H_2O/lb. wood, and the organic concentration would be 1.33%. This concentration could be compared with a value of 0.4% which would be obtained



Overall water balance: $$M = \frac{YW(1 - S_o)}{S_o} - \frac{W(1 - S_i)}{S_i} = W\left[\frac{(1 - S_o)Y}{S_o} - \frac{1 - S_i}{S_i}\right]$$

Organic balance: $$C_o = \frac{W - YW}{W(1 - S_o)/S_o} = \frac{(1 - Y)S_o}{1 - S_o}$$

Recycle required (at given ClO_2 concn.): $$R = \frac{fW}{X} - M$$

Soluble concentration with no recycle: $$C_o = \frac{1 - Y}{\frac{(1 - S_i)}{S_i} + \frac{f}{X}}$$

since $M = fW/X$ and $$S_o = \frac{1}{1 + \frac{1}{Y}\left[\frac{(1 - S_i)}{S_i} + \frac{f}{X}\right]}$$

when there is no recycle.

Figure 1. Recycle over Oxidation Reactor

if there was no recycle. Hence the concentration of dissolved material is increased by a factor of 3.33 when 71.2% of the liquor in the reactor is recycled. If the final consistency after dewatering is 20%, recycle would amount to 6.16 lb. H_2O/lb. wood, make-up water would be 2.84 lb. H_2O/lb. wood, and the organic concentration would be 1%, or an increase by a factor of 2.5. The worst case, as far as build-up is concerned, would occur if the consistency leaving was the same as the consistency entering the reactor. In this case, 9 lb./lb. recycle would be needed (100% liquor recycle) and no make-up would occur. The organic concentration would be 4%, a tenfold increase over the value for no recycle.

More important than the numbers given above are the relationships between variables. All water which moves with the wood ultimately shows up as dilution of the final spent liquor. Thus, although the build-up in concentration could be minimized by entering the reactor at low consistency, the water entering in the low consistency feed would cause a dilute spent liquor. The value of soluble concentration is determined only by the stagewise yield and the consistency after dewatering. However, exit consistency is related directly to make-up requirements, and the relative increase in concentration of dissolved materials is related directly to the amount of recycle, the ClO_2 requirement, and the solubility of ClO_2. For reasonably attainable values of the consistency after dewatering, the concentration of dissolved materials will be about three times greater than the concentration which would be obtained without recycle.

The time required to carry out an oxidation to the 9% consumption level with an aqueous solution of ClO_2 is about 5 hours at 35°C. This is a somewhat longer time and would be carried out at a slightly lower consistency than that used in present ClO_2 bleaching. It appears that oxidation with aqueous ClO_2 could be carried out in equipment essentially the same as that used for bleaching with ClO_2. The towers may be expected to be about twice the size as for a comparable bleaching

tonnage. Further kinetic data on oxidation with aqueous ClO_2 are needed before a more accurate sizing of the reactor could be made.

Gaseous Oxidation

As has been mentioned previously, it is possible to carry out the oxidation by contacting moist shredded wood with a gas stream containing ClO_2. The moisture plays a critical role since ClO_2 gas will not react with dry wood to an appreciable extent. A study of the effect of moisture level on the reaction between wood and ClO_2 gas has not been carried out. Sufficient work has been done, however, to determine that a water-to-wood ratio of 1:1 is adequate. Since this is about the level of moisture after the fiberization step, it is feasible to consider gaseous oxidation immediately following the fiberization of the wood.

It has proven difficult to study the reaction of gaseous ClO_2 with moist shredded wood in the laboratory, mainly due to problems in obtaining a uniform reaction over a portion of fiberized wood. The most successful results were achieved with a continuous reactor, in which both the shredded wood and the gas passed continuously through the reactor. The apparatus used and the results obtained are presented in Progress Report Five, "Continuous Pulping with Gaseous Chlorine Dioxide."

A good correlation was found between oxidation with gaseous ClO_2 and oxidation with aqueous ClO_2. In particular, the relationship between the amount of ClO_2 consumed and the amount of lignin removed during oxidation-extraction was essentially the same for each case. There appears to be no reason for believing that chemical requirements found in the more easily performed aqueous ClO_2 experiments cannot be applied to the gaseous case. Thus, for example, aspen can be oxidized with an amount of gaseous ClO_2 of 9% on the original wood in a single stage and after extraction yield a substantially delignified pulp.

One significant difference between gaseous and aqueous oxidations is that the gaseous reaction occurs more rapidly. It is believed that the reason for this increase in reaction rate is that in the gaseous case the ClO_2 solution is formed very close to the reaction site (right in the moist wood) and thus the paths for diffusion of ClO_2 in solution are reduced. It appears that ClO_2 gas can be reacted to the extent of 9% on the wood in about 15 minutes at a temperature of 45°C. This may be compared to several hours with aqueous ClO_2 at 35°C.

Caution must be exercised when dealing with these apparent reaction times. No detailed kinetic studies have been made for either the aqueous or the gaseous case, and rate constants are not available for direct comparisons. Some of the differences are operational in nature. The aqueous oxidations were carried out to nearly complete exhaustion of the oxidant. Since the reaction would be expected to slow down as the ClO_2 becomes used up, a significant portion of the total time was used up during the period of approaching exhaustion. The nature of the continuous gas reactor, on the other hand, required passing a goodly amount of ClO_2 through in order to get the desired degree of consumption. Hence, the gaseous experiments never did include a period of approaching exhaustion of chemical. In addition, the residence time of shredded wood in the reactor could not be accurately measured. Thus, although it definitely appears that the gaseous oxidation occurs more rapidly, it is difficult to assign a quantitative value to the difference in rate.

One of the potential problems with gaseous oxidation is that there is relatively little water present to dilute the acids formed (e.g., HCl) as the oxidation proceeds. Thus, the pH of the water on the wood will drop to very low values (less than 1) as the reaction proceeds. This leads to the possibility of acid attack on the fibers. Work done to date indicates that this is not a severe problem if the reaction time and temperature are kept to a sufficiently low level.

One problem with the use of a gaseous oxidation is that there does not appear to be existing equipment which could be used for carrying it out. Thus, gaseous oxidation requires the development of a reactor. The work on the laboratory reactor indicated the problems which would be involved in such a development. Basically, they are problems of feeding and maintaining wood flow through the reactor while at the same time having uniform contact with the gas flow. These problems are associated with the handling characteristics of the fiberized wood. No work on the development of such a reactor is currently in progress under this project. It is thought that the current interest in gas-phase pulp bleaching might lead to equipment which could be readily adapted for oxidation of fiberized wood with gaseous ClO_2. Interest in the development of such a reactor would increase enormously if the aqueous alternative should prove unfeasible.

Oxidation Summary

The present state of knowledge concerning the oxidation step can be summarized as follows. The oxidation can be carried out either with an aqueous solution of ClO_2 or by passing gaseous ClO_2 over moist shredded wood. The amount of ClO_2 required to achieve substantially complete delignification is about 9% based on the incoming wood. This can be reduced to about 7.5% by using two oxidation stages with an intermediate alkaline extraction.

The advantages of using aqueous-phase oxidation include the following:

(1) It is more firmly based on laboratory-scale experiments. The great bulk of the experimental work has used aqueous ClO_2 solutions. Hence, there is reason for confidence that this technique will work on a commercial scale.

(2) The equipment presently used for bleaching pulp with ClO_2 solutions could be readily adapted to oxidation of fiberized wood with aqueous ClO_2.

(3) It may permit the oxidation to proceed with less acid attack on the fibers.

The disadvantages of using aqueous-phase oxidation include the following:

(1) The low solubility of ClO_2 in water requires that the aqueous oxidation be carried out at low consistency. This leads to an unacceptable dilution of final spent liquor unless the oxidizer liquor is recycled to the ClO_2 absorber. This recycling of spent liquor may affect the efficiency of the oxidation.

(2) There is a relatively slower reaction rate compared to the gaseous case.

The advantages of using gaseous oxidation are the following:

(1) The reaction rate can be carried out directly on the fiberized wood without the addition of water. Thus, there is no dilution of spent liquor.

(2) The relatively rapid reaction rate permits closer control of and more rapid response to changes in the oxidation step. Less hold-up of material is involved.

(3) There is no need for the reactor to withstand hydrostatic pressure.

The disadvantages of using gaseous oxidation include the following:

(1) It is less firmly based on laboratory work. Additional laboratory-scale work would be required to achieve the same degree of confidence in the process as exists with aqueous oxidations.

(2) It requires the development of a reactor for carrying out the operation. This could be a troublesome problem because of the handling characteristics of fiberized wood.

(3) There may be damage to the fibers due to the low pH on the wood as oxidation proceeds.

One of the additional factors involved in this comparison is the compatibility of either method with the ClO_2-generation system. This problem will be discussed in detail later in this report.

Extraction

The alkaline extraction permits the solubilization of the oxidized lignin, and hence its removal from the wood. By far the bulk of the material removed comes off during extractions. Delignification is achieved through the combination of the oxidation and extraction steps. The oxidation is carried out only to the point at which the oxidized lignin is soluble in alkaline solution. The alkaline extraction then removes this material from the wood.

A rather thorough study of the alkaline extraction step has been carried out and the results were presented in Progress Report Six. It was found that the alkaline extraction exerts a considerable effect on fiber properties. Alkali extraction conditions influence yield, unbleached fiber properties, fiber liberation, removal of modified lignin, and retention of carbohydrates.

The effects of temperature, time, and consistency on the extraction behavior were studied. Increasing the temperature from 40 to 60°C. increased the rate of removal of modified (oxidized) lignin. Increase in temperature did not appear to increase the removal of polysaccharides. The time that the extraction is carried out plays a significant role. The initial rate of removal of modified lignin is quite high. The residual lignin content approaches a constant value as time proceeds. Polysaccharide material is removed as extraction time increases.

Ease of fiber liberation also increases as extraction time increases. Increase in consistency had a positive effect.

Because of this previous work, the conditions for the alkaline extraction are quite well defined. For a single-stage oxidation extraction, using 9% ClO_2 on the original wood, about 10% NaOH is required. If sequential oxidation-extraction stages are used, it is expected that the caustic requirement will follow the amount of oxidant used. These extractions would be carried out at temperatures of 60-70°C. for times up to an hour. They would be carried out at as high a consistency as practical.

Equipment for carrying out the alkaline extraction is readily available. There appears to be no major reason why the same type of equipment used for extractions in bleaching sequences could not be readily adapted for alkaline extractions in holopulping. The time and temperature requirements are similar, and the consistency range could also be comparable. Because the solubility of NaOH is very high, the consistency in the extraction step is not controlled by the chemical requirements, but rather by the ability to mix the chemicals with the oxidized fiberized wood and maintain proper flow in the towers. Accordingly, it is expected that towers for the alkaline extraction step would be about the same size as extraction towers for bleaching at a comparable tonnage.

The problem of dilution is present in the alkaline extraction step, as it is with all steps in the pulping process. The problem is not as severe as with aqueous-phase oxidation. However, the extraction must be carried out at conditions which minimize the introduction of additional water into the system. Basically, this means either carrying out the extraction at very high consistencies (20-30%) or recycling liquors around the extraction zone. Because of the difficulties in

achieving uniform mixing of chemicals at high consistency, the latter procedure appears to be more practical.

Recycling liquors around the alkaline extraction may affect the extraction process. The bulk of the material which is removed from the wood is solubilized in the extraction step. Thus, the concentration of dissolved organic and inorganic compounds will be relatively high and will be increased significantly by recycling. This could cause an increased consumption of caustic. Although the cost of additional caustic is not as expensive as overconsumption of ClO_2, it would constitute an increased economic burden on the process. Even more important, perhaps, is that a high concentration of soluble material may affect the progress of the extraction itself. Since the extraction plays a significant role in the ultimate determination of pulp properties, any interference with the extraction could be critical.

Hypochlorite Treatment

The hypochlorite treatment serves a dual role in the process. It exerts a marked whitening or bleaching effect and aids in the separation of individual fibers. A single-stage hypochlorite treatment after oxidation and extraction is able to raise the brightness of the pulp into the 80 GE brightness range.

The amount of hypochlorite required is about 3% by weight on the original wood (expressed as available chlorine). The data are somewhat inconclusive on the need to buffer the hypochlorite, although the treatment is definitely carried out on the alkaline side. The conditions presently being used for this step are temperatures of about 40°C. and times from one to three hours. Consistency can be considered to be a variable determined primarily by considerations of reactor design and ability to mix chemicals with the pulp.

The conditions used for carrying out the hypochlorite step in holopulping are similar to conditions for hypochlorite bleaching. Thus it appears that the same equipment used for hypochlorite bleaching could be used in holopulping. Sizes would be comparable for comparable tonnages.

The problem of liquor dilution and recycling is present in this step as in the others. The same general comments apply. An additional factor at this stage is the degree of cleanliness required for the pulp entering the hypochlorite step since this will determine the need for washing after the extraction step. In essence, the greater the effect that dissolved materials have on the hypochlorite treatment, the more stringent the requirements on washing before hypochlorite and the greater the ultimate dilution of the spent liquor.

Washing

As is evident from the preceding discussion, the tendency toward spent liquor dilution in a multistep pulping process is severe. This introduces a powerful constraint on the amount of washing which can be tolerated if the spent liquors are to be processed rather than to be sewered. In view of the present concern with the environment and the undoubted direction which this concern is leading toward, sewering of spent liquors is not considered a practical alternative in a new pulping process. Hence the process must be able to "live" with the constraints on washing.

Washing and the general problem of the water balance over the pulping process will be discussed in much greater detail when considering spent liquor processing. At this point, attention is confined to the effects of washing constraints on the pulping process itself. There are essentially two ways by which the amount of water added to the system in washing can be minimized. The first is to eliminate as many washing steps as possible. The second is to recycle the wash liquors through the process in a countercurrent manner so that the same water is

used several times. The latter method has the disadvantage that concentrations of materials in the washing liquor build up so that the degree of cleanliness of "pulp" after washing is decreased. At any given level of spent liquor concentration the amount of water available for washing is increased as the amount of water added in the pulping sequence decreases. This is the reason for liquor recycling and/or high-consistency operation in the individual pulping steps.

The ultimate determination of the amount of washing which can be carried out will be determined by an economic balance between the cost of concentrating the spent liquor and the cost of increased chemical consumption and degraded performance in the pulping steps consistent with a given degree of cleanliness in the pulp leaving the process. In order to make this determination, it is vital to obtain data on the effects of liquor recycling and solubles concentration on the efficiency of the pulping steps as well as data on the degree of need for interstage washing.

Pulping Process Variations

The preceding discussion has centered on a basic pulping process involving the sequence of fiberization, oxidation, extraction, and hypochlorite treatment (F-O-E-H). There are many possible expansions on this basic sequence, some of which will be considered below. It must be borne in mind when considering these variations that the addition of more steps in the pulping process aggravates a serious situation regarding the water balance. Very careful analysis will be required to determine the overall benefits of variations in the basic process. This will be especially complicated when the benefits are subtle improvements in product quality.

It has already been mentioned that the chlorine dioxide requirement can be reduced by about 16% if the oxidation is carried out in two stages with an intermediate alkaline extraction. There is some evidence to indicate that this

may also lead to a slight improvement in the bleachability of the pulp. In this case, the complete pulping process could be described by the sequence F-O-E-O-E-H. This variation requires two more steps than the basic process, with the attendant introduction of additional water. More significant, however, is the question of the degree of washing required between the first extraction and the second oxidation. Solubles concentration in the liquor from the first extraction will be relatively high, and could exert a significant effect on the second oxidation unless removed by washing. In addition, since oxidations are carried out on the acid side, and the extraction liquors are alkaline, the change in pH between stages could result in the reprecipitation of materials on the fiber in the second oxidation.

Another variation which has been studied rather extensively in the laboratory is the use of an alkaline extraction prior to the oxidation step (alkaline conditioning). In this case, the pulping sequence is F-E-O-E-H. In some respects the alkaline pretreatment is a hangover from earlier work on chips, but there is evidence that it does have some effect on the process. The same basic problems are inherent here, namely, more water addition and the possible requirement of washing before the oxidation stage.

The preceding remarks are directed to the use of hardwoods. If softwoods are used, it is likely that an alkaline pre-extraction will be required in order to remove the resinous material and other extractives prior to any oxidation step. In this situation it is likely that the liquors from this pre-extraction would be handled separately from the spent liquors from the rest of the process since they could have a much higher by-product potential. A rather thorough washing before the oxidation would probably also be required. Since most of the work on this project has been concerned with hardwoods, the complications introduced into the overall process by the use of softwoods will not be considered in this report.

The similarity between the holopulping process and present-day bleaching practices leads to the temptation to consider the same degree of variations in approach as are used in bleaching. Caution must be used to avoid pushing the analogy with bleaching too far. Present-day bleaching is essentially an open system with respect to effluent, whereas holopulping must operate on an essentially closed basis. Hence, the constraints operating to simplify the holopulping sequence are much stronger than those operating in pulp bleaching. To put the holopulping process in its proper perspective with regard to complexity of sequences, one might well consider the effect on bleaching methods if sewering of bleach effluent was no longer permitted.

SPENT LIQUOR PROCESSING

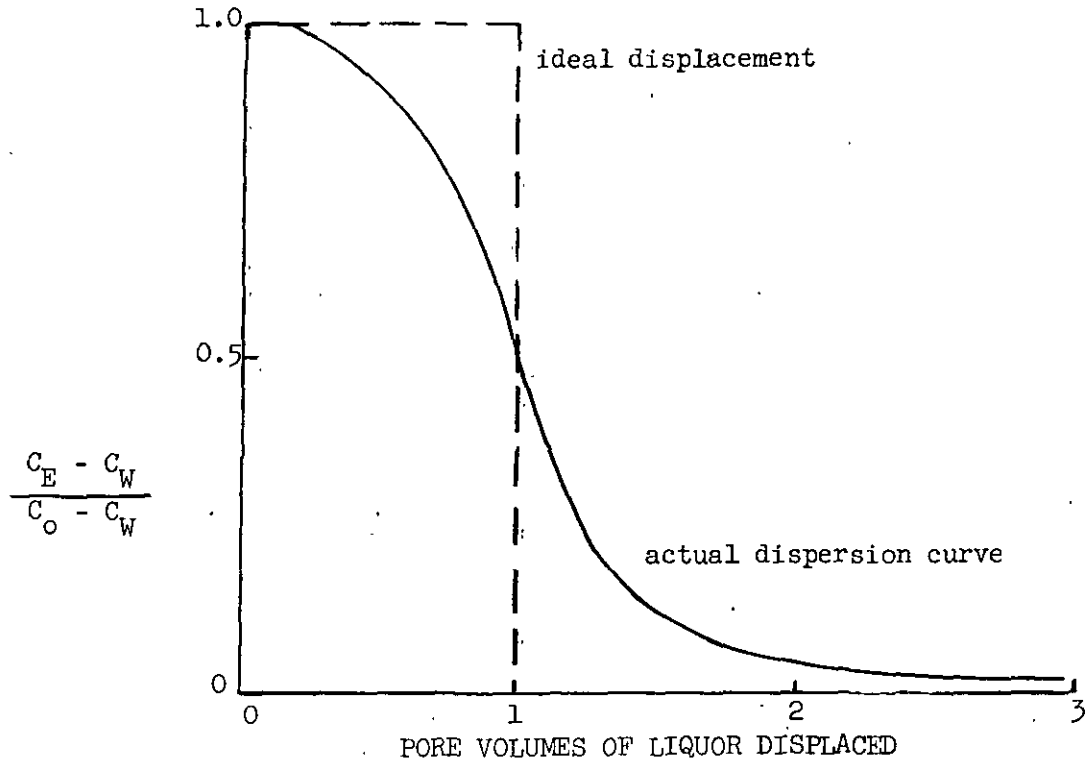
In the presently envisaged holopulping process, the spent liquors (and wash liquors) from the pulping step will be collected, concentrated by evaporation, and burned. The sodium and chlorine content of the spent liquor would be recovered in a form suitable for the regeneration of the pulping chemicals, and the heat of combustion of the concentrated liquor used to generate steam. The sequence of events involved in these operations are discussed under the heading of spent liquor processing.

Any consideration of spent liquor processing begins with a water balance over the pulping step. The water balance determines the concentration of the weak spent liquor, the amount of evaporation required to concentrate the liquor, and has a profound effect on the economics of the entire process. The water balance is profoundly affected by the washing operation. Accordingly, before considering the water balance in detail, it is necessary to consider some of the fundamental aspects of pulp washing.

Washing

Washing of pulp can be considered to consist of three basic mechanisms: displacement, dilution and thickening, and diffusion. Displacement occurs when the washing liquid (e.g., water) flows through the fiber network and physically displaces the concentrated liquor from the network. Ideally, displacement does not cause any dilution of the concentrated liquor. The operation is simply one of replacing liquor by wash liquid. Washing by dilution and thickening involves a sequence of steps of adding wash liquor to the pulp and expressing it out again. The concentration of the liquor is determined by how much dilution water is added relative to the water originally present. The degree of solids removal is determined by the amount of water expressed relative to that left in. Diffusion is involved to a greater or lesser extent in each of the above mechanisms. Diffusion is responsible for transport of soluble material from within the fiber itself and from inaccessible areas of the fiber network to areas where removal by the other mechanisms is possible. Because diffusion is an inherently slow process, time must be allowed for diffusion to take place when it is an important mechanism.

The dispersion curve is a useful means for characterizing displacement washing. A typical dispersion curve is shown in Fig. 2. The curve for an ideal displacement is also shown. A dispersion curve could be generated by permeating a fiber network containing liquor with water and measuring the concentration of the liquor leaving the pad as a function of the amount of permeation done. If the action was pure displacement with a sharp interface between the wash water and the liquor being displaced, the result would be the ideal curve shown in Fig. 2. Actual curves deviate considerably from the ideal, due mainly to channeling and diffusion. Wash water tends to pass through larger pore spaces more rapidly and "breaks through" before displacement is complete. The dispersion curve can be used to determine



C_o = initial concentration of solubles in pulp mat

C_W = concentration of solubles in wash water

C_E = concentration of solubles in liquor leaving pad

Note: At high consistency, one pore volume is less water than at lower consistency.

Figure 2. Typical Dispersion Curve

the degree of pulp cleanliness and spent liquor concentration as a function of wash water used.

Dilution and thickening can be characterized by straightforward material balances, by assuming that the soluble constituents are associated with the water present with the pulp. Then the concentration of material leaving with the pulp is the same as the concentration of solubles in the spent liquor, and the ratio of water remaining with the pulp to the total amount of water present determines the ratio of solids remaining to the total solids present. A summary of the material balance equations for washing by dilution and thickness is given in Table I. It can be seen that the major factors influencing washing by this method are the amount of water added with respect to the water originally present, final consistency, and concentration of wash water.

This discussion on washing has been presented to provide for understanding the problems of holopulp washing. It is believed that holopulp washing requires a higher degree of effectiveness than conventional pulp washing and involves more complexity. Specifically, the questions which must be asked here are twofold: How do various commercial washing methods relate to washing efficiency, amount of water needed, liquor concentration, and constraints, if any, on reactor consistencies? How do reasonable washing methods affect the water balance over the pulping process?

TABLE I

MATERIAL BALANCE EQUATIONS FOR WASHING BY DILUTION AND THICKENING

Definitions:

S_i = consistency pulp initial (before dilution)

S_o = consistency after dilution and thickening

D = wash water used, lb. water/lb. pulp

L = spent liquor obtained, lb. water/lb. pulp

C_i = inlet solids concentration, lb./lb. water

C_o = outlet solids concentration, lb./lb. water

C_w = concentration solids in wash water, lb./lb. water

Water balance: $L = 1/S_i - 1/S_o + D$.

Solids balance: $C_o = \{[(1/S_i) - 1]C_i + DC_w\}/\{[(1/S_i) + 1] + D\}$. (concn. of spent liquor)

Washing efficiency: $$\text{Efficiency} = 100\% \left[1 - \frac{(1-S_o)S_i}{(1-S_i)S_o} \frac{1 + \frac{S_iD}{1-S_i}\frac{C_w}{C_i}}{1 + \frac{S_iD}{1-S_i}} \right].$$

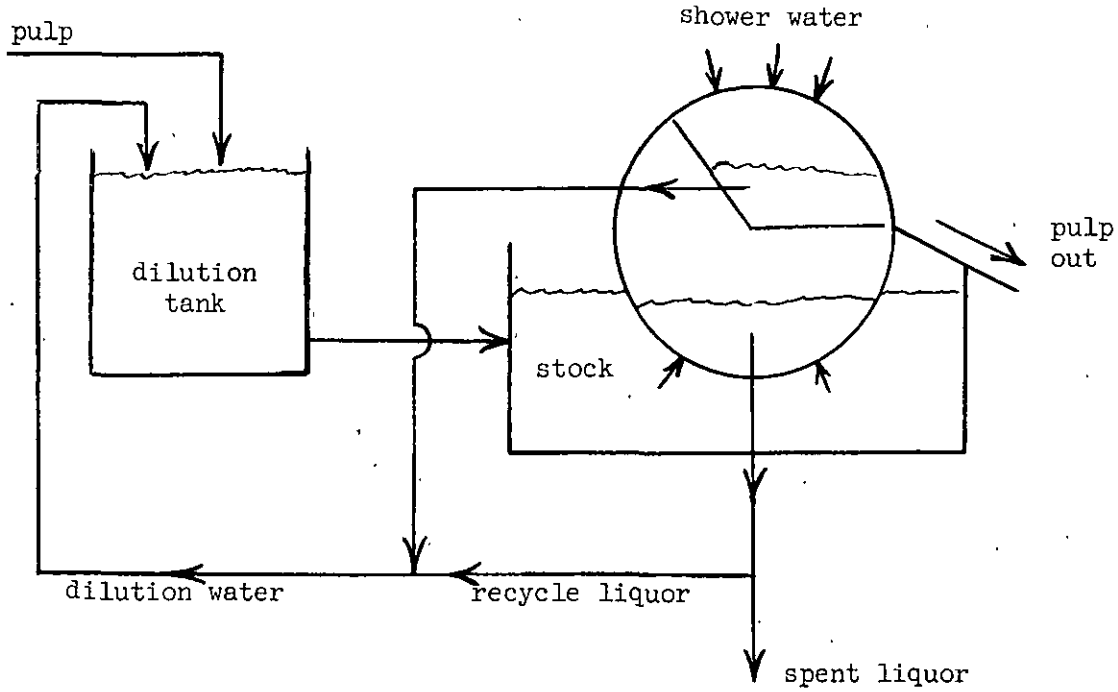
Special case: Consistency brought back to same level, $S_i = S_o = S$.
Pure water used for washing, $C_w = 0$.

$$\text{Efficiency} = 100\% \left[\frac{\frac{S_iD}{1-S_i}}{1 + \frac{S_iD}{1-S_i}} \right] = 100\% \left[\frac{D}{\frac{1-S_i}{S_i} + D} \right] = 100\% \left[\frac{\text{water added}}{\text{original water} + \text{water added}} \right].$$

Filter Washers

Drum washers or filter washers involve all three basic washing mechanisms. Dilution and thickening is involved as the mat is formed on the drum, and displacement occurs as the pulp mat is washed on the drum. A schematic diagram of a single drum washer and a block diagram for a model of this washer are shown in Fig. 3. The material balance equations are shown in Table II. Examination of the model and the equations yields some interesting findings. In the case where one of the objectives of the washing operation is to achieve as high a spent liquor concentration as possible, the amount of water entering must be kept to a minimum. Thus, recycled spent liquor must be used to dilute the pulp down to the consistency required in the stock pit. Because of this high recycle requirement, the washing effectiveness achieved by the dilution and thickening step is greatly lessened. The dilution and thickening step reduces the concentration of solids on the pulp from X_i to X_L, and the displacement starts at a concentration X_L. Thus the closer the spent liquor concentration is brought to the inlet concentration (as is desirable from a recovery standpoint) the more the washing burden is shifted to the displacement portion of the cycle (i.e., the showers on the drum). Thus when considering drum washers for the holopulping system, attention must be focused on the displacement washing efficiency.

Since the key washing in a drum washer system operating such as to maintain a high-solids-concentration liquor is displacement washing on the drum, the consistency on the drum is the consistency that determines the amount of wash water to be added. Even if an ideal displacement is assumed, the wash water added would equal the amount of water on the drum at the given consistency. A dewatering step after the drum would be only partially effective in removing residual materials. Since the consistency on the drum would normally run about 15%, there is some doubt



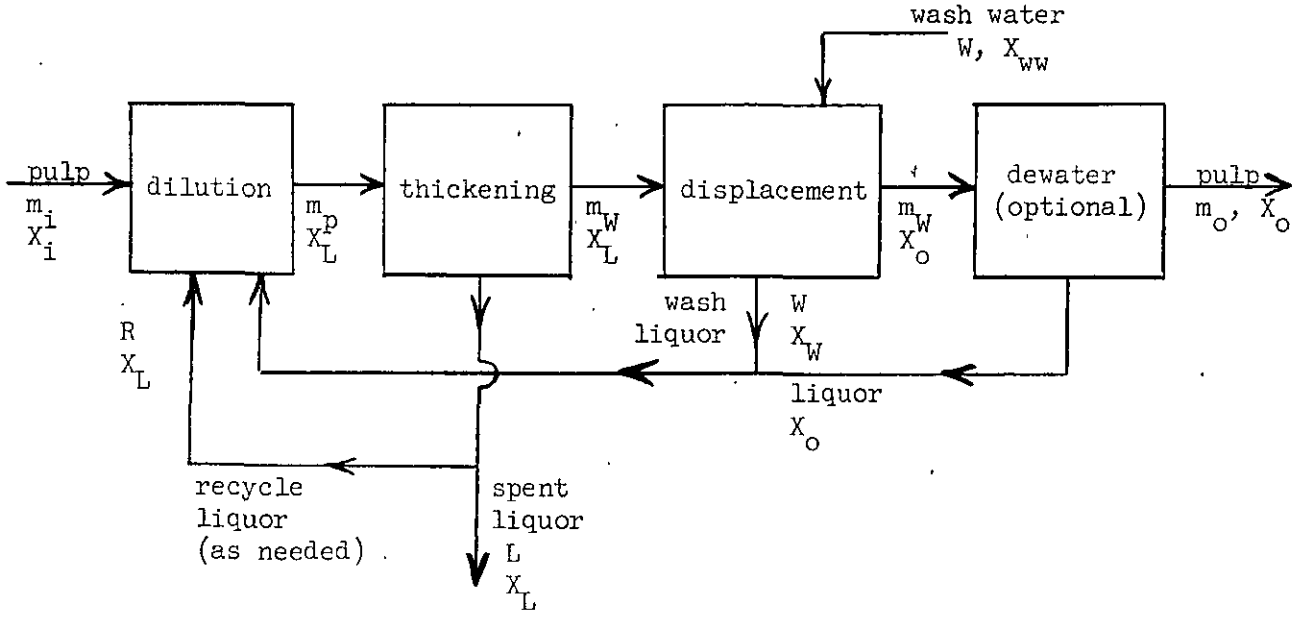


Figure 3. Schematic Diagram and Model for Drum Washer

TABLE II

MATERIAL BALANCE EQUATIONS FOR DRUM WASHER

The following quantities are defined relative to Fig. 3:

M_i = moisture of incoming pulp, lb./lb. pulp

M_p = moisture of stock after dilution, lb. water/lb. pulp

M_w = moisture on drum after dewatering, lb. water/lb. pulp

M_o = moisture of pulp out, lb. water/lb. pulp

W = wash water, lb. water/lb. pulp

L = spent liquor out, lb. water/lb. pulp

R = recycled spent liquor for dilution, lb. water/lb. pulp

X_i = concentration solids at inlet, lb. solids/lb. water

X_{ww} = concentration solids in wash water, lb. solids/lb. water

X_o = concentration solids at outlet, lb. solids/lb. water

X_L = concentration solids in spent liquor, lb. solids/lb. water

Relevant material balance equations are:

Overall water balance: $L = M_i - M_o + W$.

Dilution tank water balance: $R = M_p - M_w - L$.

Displacement washing: $\dfrac{X_o - X_{ww}}{X_L - X_{ww}} = 1 - \alpha$; α = washing efficiency .

$\alpha = f(W, \text{etc.})$ and could be found from a dispersion curve.

Solids balance: $X_o = X_{ww} + \dfrac{(1 - \alpha)M_i(X_i - X_{ww})}{M_i + W - \alpha M_o}$,

and $X_L = X_{ww} + \dfrac{M_i(X_i - X_{ww})}{M_i + W - \alpha M_o}$.

concerning the effectiveness of drum washer systems in a process where reactor consistencies are maintained between 20 and 30%.

Drum washers of this type can, of course, be multistaged. The pulp and wash water then flow countercurrent to each other through the several stages. The washers are interconnected so that the spent liquor from one stage becomes the wash water for the preceding stage. The material balance equations presented in Table II are readily adaptable to the multistage case and can be utilized in analysis of washer configurations.

Diffusion Washers

In a sense, the term "diffusion washer" is a misnomer. The basic action in these devices is displacement. However, the displacements are carried out at a slow rate so as to allow time for the necessary diffusion to occur. Commercial equipment (e.g., by Kamyr) is available for carrying out diffusion washing on a continuous basis. These may be designed so that the wash water flows countercurrent to the pulp, so only a single stage is needed. Washers of this type can be analyzed in terms of the concept of the dispersion curve. They are capable of operating at reasonably high consistencies.

Press Washing

Press washing depends principally on the operation of dilution and thickening. Presses are used to dewater dilute stock suspensions. In order to achieve efficiency, several cycles of pressing and rediluting are required. These are arranged so that the wash liquor passes countercurrent to the pulp. Under the proper circumstances, these operations can be carried out at quite high consistencies. The material balance equations presented in Table I can be readily adapted to handling press washing.

Washer Selection

The selection of the type of washing system to be used for holopulping would be determined by economics. Specifically, the capital and operating costs of the various methods would be balanced against the degree of washing and spent liquor concentrations which they are able to produce. These cost-benefit calculations remain to be done. This problem should be quite amenable to attack by mathematical modeling. The washing equations must be incorporated into a process model to determine the effect on the water balance of the process. In order to make these calculations, some information on the characteristics of washing liquors from holopulps at the various stages is needed. Experimental dispersion curves would meet this need. In addition, some data on the flow resistance of the material would also be required.

The procedure for carrying this out would be as follows. The experimental data and suitable washer material balance equations would be used to generate curves of washing efficiency versus dilution for various washer types and configurations. These would then be used in a process model to determine the effect on the water balance. Economic evaluations would then be made. Much of the modeling work has already been done. However, the calculations have not yet been carried out because the necessary data on washing characteristics and on interstage washing requirements are not yet available.

Water Balance

The water balance over the pulping elements and the resulting effect on the concentration of the recovered spent liquor play a vital role in the economics of the holopulping process. The water balance depends upon both the pulping operations themselves and the washing operations. Pulping and washing variables are

highly interrelated as far as the water balance is concerned. Proper integration of washing with the various pulping steps is necessary in order to achieve an optimum spent liquor concentration.

In considering the overall water balance, it must be borne in mind that the more water added to the system the greater the dilution of the spent liquor. This dilution is independent of whether the water is added as a part of a pulping operation or as part of a washing step. In general, water added for washing is useful for removing the soluble material from the pulp, whereas water added in a pulping step has no material removal value. Thus a desirable goal is to reduce the amount of water added in the pulping steps to a minimum compatible with successful pulping (e.g., by recycling liquors around the pulping process elements as discussed previously) in order to conserve water for use in washing. This objective is the basis for the study of the water balance.

Consider water addition in the pulping operations themselves. Water serves three purposes in the various steps in the pulping sequence. These are:

(1) transporting chemical into the reactor,

(2) adjusting pulp to proper consistency for handling within the reactor, and

(3) providing a medium for the solubilization of material removed from the wood.

Confining attention to the water within a reactor, this water arises from three sources. These are as follows:

(1) water entering the element with the wood (or pulp) feed,

(2) water from recycling of liquor, and

(3) water added to the pulping system.

In considering the water balance, the major item of interest is the water added to the system. In this connection, it should be noted that in a pulping process consisting of a sequence of operations the water entering a given block with the feed is the sum of all upstream water additions, including the water entering with the shredded (or fiberized) wood.

In any given block (such as oxidation, extraction, etc.) the amount of water which must be added is dependent on a number of things. The following factors are the most important in determining the necessary water addition:

1. Chemical requirements for the given operation.

2. Dewatering limitations after the operation.

3. Interference with the pulping reactions by soluble materials.

In essence, these are parallel restraints. Whichever factor requires the greatest water addition is the controlling factor.

The amount of addition of water due to chemical requirements depends on the amount of chemical needed and the form in which the active chemical is available. For example, if an extraction requires 10% NaOH on the incoming "wood," and the caustic is available as a 50%-by-weight aqueous solution, the water addition would be 0.1 lb. of water per pound of "wood." A similar relationship between the chemical requirement and the available concentration holds for the hypochlorite step. This factor is not present in the oxidations. If gaseous-phase oxidations are carried out, no water is necessary to bring in the oxidants. If aqueous

solutions are used with recycled liquor being sent to the absorber (the only feasible approach), then the water added is determined by the difference between the amount required by stoichiometry and ClO_2 solubility and that available in the recycled liquor. Since the amount of recycled liquor available is determined solely by the dewatering limitations and possible reaction interference, factors 2 and 3 control water addition for aqueous oxidations.

Factors 2 and 3 control the amount of recycled liquor available for any given operation. These factors operate for aqueous-phase oxidations, alkaline extractions, and hypochlorite treatments. Dewatering limitations (factor 2) directly affect the amount of recycled liquor. The liquor which is recycled in an operation is obtained by increasing the consistency of the stock (dewatering) from the lower value which exists in the reactor to some higher exit consistency. The value of this exit consistency will depend on the dewatering device used (decker, drum filter, screw press, centrifuge, etc.) and the water retention and drainage characteristics of the pulp. The higher the exit consistency, the greater the portion of water which is recycled and the lower the amount of additional water needed.

Whenever a portion of the liquors is recycled over an operation, the concentration of soluble materials will increase in this liquor. This increase in concentration of the liquors may adversely affect the pulping operation either by consuming a portion of the cooking chemicals (thus causing increased chemical consumption) or by directly interfering with the pulping reactions themselves. If the adverse effects of a concentration build-up are severe enough, then recycle must be reduced and the water requirement met by water addition.

Consider now the water requirements for washing. The exact relationship between the amount of water added and the degree of washing obtained will be

dependent on certain pulp characteristics and the particular washing system employed as has been discussed in a previous section. For the purpose of this discussion, it is merely necessary to note that such a relationship is present and that, in general, washing effectiveness is increased as water used is increased, but in a highly nonlinear manner. A point of diminishing returns is reached when the use of more water has little benefit on increased washing.

In integrating washing into the pulping process, the major requirements are to determine the locations where washing is needed in the sequence and to define the wash water-spent liquor circuit. Washing would, of course, be done at the end of the pulping sequence, both to provide a clean product and to maximize the recovery of cooking chemical and dissolved organic. However, since holopulping involves a sequence of distinct steps, it is possible that washing between these steps (interstage washing) may be needed. The degree of interstage washing required will depend on the tolerance of the pulping operations to dissolved materials in general and to the impact of the liquors from one step to a subsequent step in particular (e.g., oxidizing in the presence of alkaline extraction liquors). The need for interstage washing derives from the pulping operations themselves.

In order to illustrate these factors which have been discussed and to show the order of magnitude of the general water balance problems, calculations are presented for several cases. These cases should be considered illustrative in nature and do not, in general, signify preferred values of variables.

Several assumptions are made in making these calculations. Only the organic fraction of the liquors is involved in the calculations, and the increase in organic content of liquors is equated to the yield loss in the pulping step. This simplifies the calculations since it eliminates keeping track of sodium and chlorine and avoids the problem of water production or removal by chemical reaction.

This assumption is adequate for the illustrative nature intended here. The solids in the final spent liquor could be estimated by assuming an organic-to-inorganic ratio of 2 to 1.

Washing is arbitrarily handled by assuming a washing efficiency of 95% at a dilution factor of 3. The washing efficiency is defined by

$$\text{eff.} = \frac{X_i - X_o}{X_i - X_{ww}}$$

where:

X_i = concentration of soluble material entering washer with pulp, lb./lb. water,

X_o = concentration of soluble material leaving with pulp, lb./lb. water, and

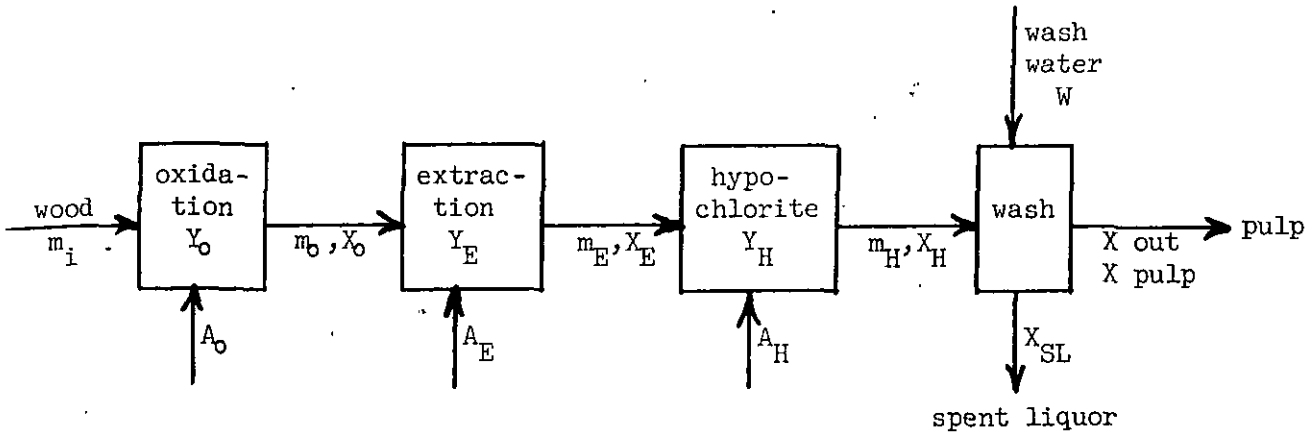
X_{ww} = wash water concentration, lb./lb. water.

This definition reflects the fact that the pulp cannot be washed any cleaner than the wash water available. The dilution factor is defined as the amount of diluting water per pound of pulp entering the system as fresh water. Diluting water is the excess water over that required to simply displace the water entering the washer with the incoming pulp. It is assumed the pulp leaves the washer at the same consistency at which it enters.

The simplest case which can be considered is the sequence oxidation-extraction-hypochlorite wash. A schematic diagram and the basic material balance equations are presented in Table III. Recycled liquor within a block is not shown. Conditions are for materials entering and leaving the blocks. These equations were used to calculate values for several cases, the results of which are shown in Table IV.

TABLE III

SCHEMATIC DIAGRAM AND MATERIAL BALANCE EQUATIONS FOR O-E-H-W SYSTEM



where:

$\underline{m}$ = moisture of pulp, lb. water/lb. pulp (=1/consistency - 1),

$\underline{Y}$ = stagewise yield, decimal fraction,

$\underline{X}$ = concentration of dissolved organic, lb./lb. water,

$\underline{A}$ = water added to blocks, lb. water/lb. pulp, and

$\underline{W}$ = wash water added, lb. water/lb. pulp.

Material Balance Relations

Oxidation: $m_o = (A_o + m_i)/Y_o$; $X_o = (1 - Y_o)/(A_o + m_i)$

Extraction: $m_E = (A_E + m_o)/Y_E$; $X_E = (m_o X_o + 1 - Y_E)/(A_E + m_o)$

Hypochlorite: $m_H = (A_H + m_E)/Y_H$; $X_H = (m_E X_E + 1 - Y_H)/(A_H + m_E)$

Wash: $W = m_H + 3$ (3 is the dilution factor)

$0.95 = (X_H - X_{out})/Y_H$, or $X_{out} = 0.05X_H$

$X_{SL} = 0.95 m_H X_H/(m_H + 3)$; $X_{pulp} = m_H X_{out}$ (lb. organic/lb. pulp)

TABLE IV

ILLUSTRATIVE WATER BALANCE DATA FOR O-E-H-W CONFIGURATION

Quantity*	Case 1	Case 2	Case 3	Case 4
m_o	3.	1	4.	3.
A_o	1.94	0	2.92	1.94
X_o	0.0068	0.0204	0.0051	0.0068
m_E	4.43	3	5.86	3.
A_E	0.1	1.1	0.1	0.1
X_E	0.1033	0.1527	0.0783	0.1033
m_H	4.88	3.37	6.38	3.37
A_H	0.2	0.2	0.2	0.2
X_H	0.1097	0.1587	0.084	0.1125
X_{out}	0.0055	0.0079	0.0042	0.0061
X_{SL}	0.0645	0.0798	0.0542	0.0652
X_{pulp}	0.0268	0.0268	0.0268	0.019

Note that base on moisture and water additions changes as pulp yield drops off, i.e., they are based on amount of pulp at point where designated.

* See diagram in Table III for key to variable nomenclature.

The first case considers an aqueous oxidation with the water addition governed by an exit consistency of 25%. The water addition in the extraction and hypochlorite steps is assumed to be controlled by chemical requirements, using values of 0.1 and 0.2 for $\underline{A}_E$ and $\underline{A}_H$, respectively. In all of these cases, the stagewise yields are taken to be 98%, 70%, and 95% for oxidation, extraction, and hypochlorite, respectively. The inlet moisture is taken to be 1 lb. water/1 lb. wood.

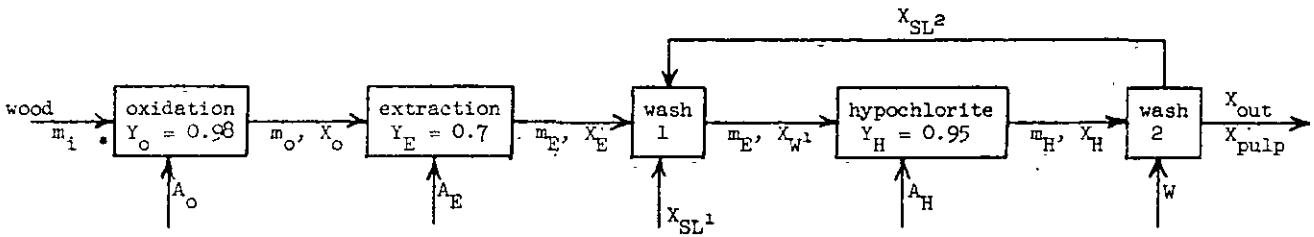
The second case is similar to the first, except that the oxidation is assumed to be carried out as a gaseous reaction without water addition, and the extraction is assumed to be controlled by dewatering to a consistency of 25%.

The third case is the same as the first case, except that the limiting consistency after the oxidation is taken to be 20%.

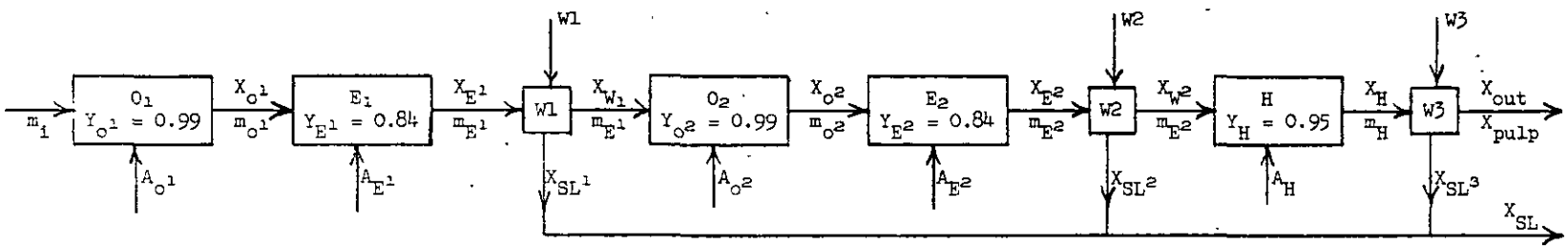
The fourth case is the same as the first. However, it is assumed that after the extraction the material is dewatered to 25% consistency and that the liquor removed here is combined with that from the wash to give the spent liquor.

All of the above cases refer to an O-E-H-W sequence and are the basis for the data in Table IV. They illustrate in general the effect of pulping process variables on the water balance. As has been mentioned previously, washer locations and wash water circuits also play a role. Three additional cases have been chosen to illustrate the effect of these variables. Schematic diagrams of these cases are shown in Fig. 4 to define the sequences, interconnections, and variable names. The results of these calculations are presented in Table V.

Case A



Case B



Case C

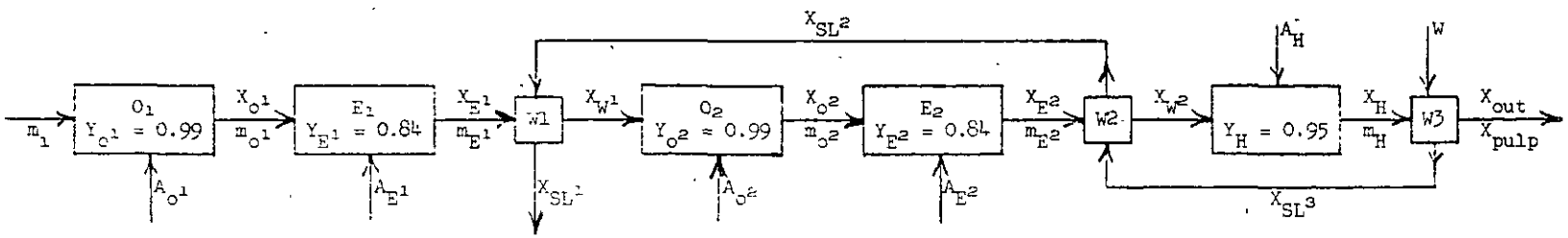


Figure 4. Schematic Diagrams for Washer Configuration Cases

TABLE V

ILLUSTRATIVE WATER BALANCE DATA FOR WASHER CONFIGURATION CASES

Quantity*	Case A	Case B	Case C
m_{o^1}	3.	3.	3.
A_{o^1}	1.94	1.94	1.94
X_{o^1}	0.0068	0.0034	0.0034
m_{E^1}	4.43	3.64	3.64
A_{E^1}	0.1	0.05	0.05
X_{E^1}	0.1033	0.0558	0.0558
X_{W^1}	0.0241	0.0028	0.0768
m_{o^2}	--	3.68	3.68
A_{o^2}	--	0.	0.
X_{o^2}	--	0.0055	0.0796
m_{E^2}	--	4.44	4.44
A_{E^2}	--	0.05	0.05
X_{E^2}	--	0.0483	0.1214
X_{W^2}	--	0.0024	0.0191
m_H	4.88	4.89	4.89
A_H	0.2	0.2	0.2
X_H	0.0339	0.0131	0.0291
X_{out}	0.0017	0.00066	0.0015
X_{SL^1}	0.0668	0.0290	0.0657
X_{SL^2}	0.0199	0.0274	0.0780
X_{SL^3}	--	0.0077	0.0171
X_{SL}	0.0668	0.0215	0.0657
X_{pulp}	0.0083	0.0032	0.0073

* See Fig. 4.

Case A is identical to Case 1 in Table IV except that two washing stages are used, and the spent liquor from the final wash is used as the wash water for the washing stage immediately following the extraction.

Case B involves a multistage pulping operation with two oxidation stages and two extraction stages. A washing stage using fresh water is placed after each extraction as well as at the end of the sequence. It was assumed that no water had to be added in the second oxidation. It was assumed that water addition in extraction and hypochlorite stages were determined by chemical requirements. The addition was evenly split for the two extractions. The yield values were picked so that the final yield figure was comparable with the previous cases.

Case C is essentially the same as Case B, except that the washers are coupled in series countercurrent to the flow of stock through the system. The spent liquor from the final wash is used as wash water for the washer after the second extraction. The spent liquor from this stage is used as wash water for the first washer, from which the process spent liquor is drawn.

Examination of these illustrative calculations gives some interesting insights into the water balance problem. Consider the data on the basic O-E-H-W configuration in Table IV. It might be noted that the spent liquor concentrations are relatively low even though the wash water was limited and the consistencies leaving the blocks were relatively high (a moisture of 4 is equivalent to a consistency of 20%). This illustrates the magnitude of the water balance problem in holopulping.

Recycling of liquors is almost mandatory in order to obtain the consistency values required. This is definitely true if aqueous-phase oxidations are used. The problem is avoided in oxidations if the gaseous method is used.

Recycle is also probably needed in the extraction and hypochlorite steps. The only alternative is to develop methods for properly mixing concentrated caustic and hypochlorite solutions with the pulp at consistencies on the order of 25%. The need for high consistencies is real. A comparison of Case 1 with Case 3 shows that a significant dilution of the spent liquor takes place when the material is dewatered to 20% rather than 25% consistency after the oxidation. Comparing the aqueous and gaseous cases (Case 1 and Case 2) shows this effect even more clearly. By delaying the dewatering constraint by one stage, a significant increase in spent liquor concentration is obtained. Case 4 shows that a slight improvement is obtained if dewatering is carried out more fully after the extraction step. The fact that only a slight improvement is obtained illustrates the need to keep all stages at very high consistencies. In essence, the need is to minimize water addition. Case A in Table V can also be compared with Case 1. This comparison favors the two-washing-stages approach since the countercurrent flow of wash liquor provides for a more thoroughly washed pulp and a slightly stronger spent liquor. Particular attention should be paid to the threefold reduction in the concentration of the hypochlorite stage achieved by the two-washes approach. This would help minimize side reaction during the hypochlorite step.

Cases B and C illustrate the dilemma of complicating the process by increasing the number of pulping operations. Case B shows that a very effective washing can be carried out interstage which would greatly minimize side reactions. Pulp residual concentrations after the washes are very low. However, this benefit is achieved at the expense of a very dilute spent liquor. Case C illustrates the fact that internal recirculation of wash water is not a cure-all for the water balance problem. The more often a given amount of wash water is used, the greater the build-up in concentration and the less effective it is as a washing medium. Case C shows this in the extreme since the build-up in concentration of the wash

water as it passes through the system is so great that the first wash stage does not wash the "pulp" but rather increases the concentration of materials on the pulp ($\underline{X}_{\underline{W}1} > \underline{X}_{\underline{E}1}$).

It should again be emphasized that these calculations are illustrative only. They do, however, clearly show the magnitude of the problem, and the type of constraints which water balance exerts on the process. More detailed and definitive calculations can be made when data on the washing characteristics of holopulp and the effects of soluble materials on pulping reactions become available.

Evaporation

After the spent liquor has been collected from the pulping system, it must be concentrated prior to combustion. It is expected that concentration would be accomplished through multiple-effect evaporation since this is a standard practice in the industry for treating waste liquors. Other concentrating methods, such as reverse osmosis, could be employed if they would provide a more economical water removal. However, it is felt that the current dominance of multiple-effect evaporators in the industry reflects the economic advantages of evaporation. Evaporation of spent liquors rests on a well-developed technology. For these reasons, current thinking on the problem of concentrating holopulp spent liquors is based on evaporation methods.

The problem of evaporating holopulp spent liquors has received little attention to date. Appendix II in Progress Report Five discussed one experiment on evaporation. A composite spent liquor was evaporated to about 50% solids at 40°C. in a vacuum rotary evaporator. The condensate was clear and colorless with a very faint chlorine-like smell. A qualitative test for chloride ions in the condensate was negative. There was no solids precipitation in the concentrated liquor.

More information is needed before the feasibility of evaporating holo-liquors can be conclusively stated. From evaporator design considerations, data are needed on the properties of these liquors. Specifically, the viscosity of the liquors as a function of solids content (and organic-to-inorganic ratio) is needed to properly size the evaporators. In addition, data on the tendency toward solids precipitation at higher solids contents are needed so that scaling tendencies can be evaluated. Data are also needed on the foaming tendency of hololiquors since this could greatly interfere with evaporation. Finally, the corrosive nature of these liquors must be investigated to provide a basis for the proper selection of materials.

From a process standpoint, other problems are present which need further investigation. It is highly desirable to use the condensate from the evaporators as wash liquor in order to conserve water and minimize effluent streams. To a large extent, this will depend on the degree of contamination of the condensate. Hence, data are needed on the amounts and types of compounds likely to be present in the condensate. The other problem has to do with noncondensable gases given off during evaporation and possible air pollution problems associated with them. It is necessary to know what compounds are present in noncondensable gases (e.g., chlorine gas) and in what amounts in order to determine if suppression measures need to be taken.

Combustion considerations in the furnace will dictate the degree of concentration of spent liquor required. The liquor must be concentrated to the point at which stable firing can be maintained. Hopefully, this will be at a level obtainable from natural circulation, LTV, multiple-effect evaporators. If not, direct-contact evaporators will have to be considered. The number of effects would be determined by economic considerations balancing the cost of evaporators versus cost of steam used to carry out the evaporation.

Combustion

The concentrated spent liquors would be burned in a combustion furnace. Suitable heat recovery equipment could be provided to recover the energy value of the organic compounds in the form of steam. The inorganic chemicals (sodium and chlorine) are to be removed in a form suitable for the regeneration of the pulping reagents. Present thinking is predicated on the inorganic combustion products being sodium chloride (NaCl) and sodium carbonate (Na_2CO_3).

The nature of the combustion products of holopulp liquors is critically important. There are two aspects of this problem. The first is the nature of the gaseous combustion products and the possibility that chlorine or chlorine compounds will be present in the flue gas. The second is the nature of solid (or molten) combustion products which are to be used for chemical regeneration. The goal of the combustion operation is to limit the gaseous products to CO_2, H_2O, N_2, and O_2, and to obtain the remaining elements as solid NaCl and Na_2CO_3 (along with any inerts to be purged from the system).

Very little work has been done to date on the products of combustion of spent liquors from holopulping. Progress Report Five describes some experiments on combustion of composite holopulping spent liquors. These were very small-scale combustion experiments carried out in crucibles in muffle furnaces at temperatures from 1000 to 1400°F. (furnace temperature). Analysis of the ash indicated that about 95% was made up of NaCl and Na_2CO_3, the remainder being an insoluble material. The relative amounts of NaCl and Na_2CO_3, and the ratio of ash to liquor solids content were compatible with the assumption that nearly all sodium and chlorine in the liquor were converted to NaCl and Na_2CO_3. However, a rigorous material balance was not made in this experiment, so that it cannot be regarded as conclusive. In these combustion experiments, no objectionable odors were detected in the gases

liberated during combustion. This is indicative that little chlorine or volatile chlorine compounds are produced by combustion. These data strongly indicate that the major products of combustion are NaCl and Na_2CO_3, and that the regeneration system should be based on these products. However, present data are not sufficiently quantitative to determine the extent to which conversion to desirable chemicals occurs nor the extent of potential air emission problems.

One way of looking at the combustion problem is to consider whether chlorine gas or hydrogen chloride is the predominant combustion product from the burning of a chlor-organic compound. The reasoning would be that in the presence of sodium compounds, hydrogen chloride would be more readily converted to NaCl than would chlorine, since the chlorine would already be in the chloride form. It is of interest to note that standard heats of combustion for chlorine-containing organic compounds are based on HCl as the combustion product. This would seemingly reflect the tendency for HCl to be formed under bomb calorimeter conditions.

A rather simple experiment has been performed to determine the tendency to form gaseous chlorine during the combustion of chloro compounds. An aspirating burner was used to combust certain chlorine-containing compounds in a flame. The combustion gases were passed through a scrubber train containing a solution of NaOH (1% NaOH). Any HCl present in the combustion gases would react with the caustic to form NaCl, thus lowering the pH of the absorbing solution. Any chlorine gas formed would react to form salt and hypochlorite. The addition of potassium iodide solution which would react with the hypochlorite to liberate iodine could then be used to test for chlorine in the combustion gases.

In initial experiments with this system, carbon tetrachloride was burned in an acetylene-oxygen flame. Combustion was continued for a length of time sufficient to lower the pH of the absorbent solution to less than 2. No

discoloration of the solution was observed when potassium iodide solution was used. These observations indicated that a substantial amount of HCl was formed with a negligible amount of chlorine gas being produced. It is of interest that the HCl had to be formed in the flame since no hydrogen atoms are present in CCl_4, the source of the chlorine.

A second set of experiments were carried out using a natural gas-oxygen flame to produce a lower temperature flame than when acetylene was used. Both chlorobenzene and carbon tetrachloride were burned in this flame. When the conditions had been adjusted to give an intense blue flame, carbon tetrachloride combustion products liberated iodine from the absorbent solution (indicating chlorine in the combustion products), while the chlorobenzene did not. When conditions were adjusted to give a yellow-white, somewhat smoky, lower temperature flame, combustion of both chlorobenzene and carbon tetrachloride liberated iodine in the absorbing flasks. The liberation was significantly increased over that occurring when the blue flame was used. A definite correlation existed between lower flame temperature and increased chlorine production.

It appears that the following interpretation can be put on these observations. The primary chlorine-containing combustion product is HCl. When sodium is present, it would be expected that the primary chlorine-containing combustion product would be NaCl. However, a potential problem of emission of chlorine gas appears to exist. It is likely that this problem becomes more severe at lower combustion temperatures. The extent of the problem remains to be determined. In particular, the effect of the presence of sodium compounds in the combustion products on the amount of chlorine present must be clarified. These experiments have served to flag a problem that is potentially very serious. Air pollution abatement requirements would undoubtedly necessitate reducing chlorine emissions to a negligible level.

Further insight into the combustion products which could be formed from combustion of holopulp spent liquors can be obtained from thermodynamic considerations. This approach has been fruitfully used in understanding the combustion of conventional spent liquors. Basically, the procedure involves assuming certain compounds which might be present as combustion products, relating these compounds through chemical reactions, and then determining the equilibria of the reactions involved. The procedure is valid only to the degree that the correct combustion products are included, and the reactions as written summarize sequences of reactions which can actually occur. However, the results of calculations of this type can indicate the species which are likely to predominate in an actual combustion operation.

Considering the combustion of a holopulp spent liquor containing sodium, chlorine, and organic compounds, it might be assumed that the combustion products, under oxidizing conditions, are CO_2, H_2O, O_2, Na_2CO_3, NaCl, HCl, and Cl_2. The major question of interest is the form of the chlorine compounds, particularly the degree to which chlorine will be tied down as NaCl. In all of this discussion of combustion of spent liquor, it is assumed that sodium is present in excess of chlorine on an equivalent basis so that it is possible to convert all of the chlorine compounds to sodium chloride.

The chemical reactions involving the chlorine atom could be written as follows:

$$H_2O(g) + Cl_2(g) \rightleftarrows 2HCl(g) + \tfrac{1}{2}O_2(g) \qquad (1)$$

$$Na_2CO_3(s) + Cl_2(g) \rightleftarrows 2NaCl(s) + CO_2(g) + \tfrac{1}{2}O_2(g) \qquad (2)$$

$$2HCl(g) + Na_2CO_3(s) \rightleftarrows 2NaCl(s) + CO_2(g) + H_2O(g) \qquad (3)$$

The first reaction would describe the distribution of chlorine compounds in the absence of sodium, and the other two would show the effect of the presence of sodium. Equilibrium constants for these reactions can be calculated from the standard free energy change at the temperature in question. This standard free energy of reaction can in turn be calculated from the standard free energies of formation which are given as a function of temperature in the JANAF Thermochemical tables. This method was used to calculate equilibrium constants for these reactions. Values calculated for the equilibrium constants at temperatures of 1100 and 1500°K. are shown in Table VI.

TABLE VI

EQUILIBRIUM CONSTANTS AS FUNCTION OF TEMPERATURE

Temp., °K.	Reaction 1 $K = \frac{P_{HCl}^2 P_{O_2}^{1/2}}{P_{Cl_2} P_{H_2O}}$	Reaction 2 $K = \frac{P_{CO_2} P_{O_2}^{1/2}}{P_{Cl_2}}$	Reaction 3 $K = \frac{P_{CO_2} P_{H_2O}}{P_{HCl}}$
1100	5.62	8.74×10^8	1.7×10^8
1500	32	3.42×10^7	1.07×10^6

These equilibrium constants can be used to predict the prevalence of certain compounds in the combustion gases. For example, the equilibrium constant for Reaction (1) can be used along with assumed values of the partial pressure of oxygen and water vapor to predict the distribution between hydrogen chloride and chlorine in the combustion gases when sodium is absent. Assuming the oxygen partial pressure = 0.04 atm. and the water vapor partial pressure = 0.2 atm., and sufficient chlorine present to give a partial pressure of 0.1 atm., if all present as HCl, it is found that at 1100°K. 96.7% of the chlorine is present as HCl. Raising the temperature to 1500°K. increases the percentage present as HCl to 99.4

These values are in qualitative agreement with the results of the flame experiments discussed previously, in which HCl was the dominant combustion product and the tendency toward chlorine formation increased as the temperature of the flame was lowered. This agreement lends credence to these equilibrium calculations.

The equilibrium constants for Reactions (2) and (3) can be used to determine the expected behavior when sodium is present. In making these calculations it is assumed that partial pressure of oxygen is 0.04 atm., that of carbon dioxide is 0.1 atm., and for water vapor 0.2 atm. At 1100°K. the equilibrium partial pressures of Cl_2 and HCl are 2.3×10^{-11} atm. and 1.1×10^{-5} atm., respectively. The values would increase by about an order of magnitude at 1500°K to 5.8×10^{-10} atm. for Cl_2 and 1.87×10^{-4} atm. for HCl.

The results of these thermodynamic calculations indicate that there should be little problem with evolution of chlorine gas during the combustion of holopulp spent liquors. At equilibrium, chlorine would be present only at the part per billion level. However, a problem of HCl evolution is present. HCl could be present in the combustion gases at concentrations of ten to several hundred parts per million. This could constitute an air pollution problem, and could also lead to corrosion problems in the furnace, boiler, and other equipment. The calculations indicate that emissions would become more severe as the combustion temperature is increased. The findings of this simplified thermodynamic analysis can be summarized as follows. The sodium and chlorine in the spent liquors will be converted primarily to NaCl and Na_2CO_3 so long as sodium is present in excess of chlorine on an equivalent basis. The major obnoxious gaseous compound produced will be HCl rather than Cl_2. It could be present in amounts which would cause an air emissions problem even though chlorine recovery (as NaCl) could run well over 99%. The emissions problem appears to worsen as combustion temperature is increased.

Another thermodynamic factor of considerable importance in the combustion of holopulp spent liquors is the state of the recovered chemicals (NaCl and Na_2CO_3). Specifically of interest are the melting points of these two materials and their volatility. The relevant data on this point are presented in Table VII. These data are quite interesting. If it is desired to operate the furnace so as to avoid molten materials, the combustion temperature is limited to 800°C., or about 1470°F. Low-temperature operation also favors low emissions from a thermodynamic standpoint. On the other hand, the furnace could be operated at temperatures well above the melting points, and the recovered chemicals removed as a molten smelt. In this case, the minimum operating temperature would be about 850°C., or about 1560°F. The factor which would limit high-temperature operation is the volatility of the salts, particularly NaCl.

Even at 850°C., the vapor pressure of NaCl is nearly 1 mm. of Hg, and it rises rapidly as temperature is increased. This volatilized NaCl would recrystallize out as it cools, for example on heat exchange surfaces. This volatility would lead to difficulties in removing NaCl from the furnace and could cause rather severe operational problems. If it is decided to carry out the combustion at high temperatures, this volatilization problem must be taken into account in the design of the furnace.

It would seem that the simplest method of avoiding difficulties is to carry out the combustion at temperatures sufficiently below 800°C. so as to avoid a potential molten state. The major difficulties in taking this option would appear to be possible problems in maintaining combustion stability and potential incomplete combustion due to decreased reaction rates. These factors remain subject to further investigation. In addition, lowering the combustion temperature will reduce the energy recovery to some degree. However, stable, complete combustion at low temperatures is the main concern.

TABLE VII

DATA ON SODIUM CHLORIDE AND SODIUM CARBONATE

Sodium Chloride

Melting point: 801°C. Boiling point: 1413°C.

NaCl Vapor Pressure Data

Pressure, mm. Hg	1	5	10	20	40
Temp., °C.	865	967	1017	1072	1131
Pressure, mm. Hg	60	100	200	400	760
Temp., °C.	1169	1220	1296	1379	1465

Sodium Carbonate

Melting point: 851°C. Dissociates:

Dissociation Pressures of Na_2CO_3

$$Na_2CO_3(s) \rightarrow Na_2O(s) + CO_2(g)$$

Pressure, mm. atm.	0.0013	0.013	0.025	0.054
Temp., °C.	700	880	1080	1200

Note: Data taken from Perry's Chemical Engineer's Handbook, 4th ed.

The combustion temperature is determined from a thermal balance involving the heat of combustion of the spent liquor and any additional fuel, the heat required to raise the combustion products up to the combustion temperature and the heat transferred to the surroundings. The heating value of the spent liquor is strongly dependent on the degree of concentration of the spent liquor. The more water present in the spent liquor, the lower the heating value and hence the

combustion temperature. If the desired furnace temperature is higher than that which can be obtained from firing spent liquor at reasonable concentrations, additional fuel can be used. Hence, a wide spectrum of combustion temperatures are obtainable by varying the degree of concentration of the liquor and the use of auxiliary fuel.

In order to make estimates of spent liquor heating values and combustion temperatures, certain assumptions have been made. It is assumed that the heating value is due entirely to the organic content of the spent liquor at 9500 B.t.u. per lb. organic. The combustion products are taken to be CO_2, H_2O, NaCl, and Na_2CO_3. The value of the combustion temperature can then be calculated by heat balance. The actual value so calculated will depend significantly on the assumed heat loss to surroundings. Table VIII presents combustion temperatures as a function of spent liquor concentration for an adiabatic case and for a case with heat loss. These values are based upon 3% excess air entering at 70°F., liquor entering at 200°F., and no added fuel. The heat loss (for that case) was taken to be 1 B.t.u. per lb. of organic burned for each degree that the combustion temperature was above ambient. The influence of liquor concentration on combustion temperature is very clearly seen in these data. It is reasonable to assume that actual furnace temperatures should fall between the two cases given in the table.

If the combustion is to be carried out at temperatures below the point at which the salt and carbonate melt, the combustion temperature would be about 1400-1450°F. It should be possible to achieve a temperature in this range by firing liquors at around 30-35% solids. On the other hand, if high furnace temperatures are desired, evaporation to concentrations of 55-60% solids may be needed. The choice of furnace temperature will have a strong influence on the degree of evaporation required and hence on the economics of the whole spent liquor processing operation.

TABLE VIII

CALCULATED COMBUSTION TEMPERATURES AS FUNCTIONS OF CONCENTRATIONS OF SPENT LIQUOR

Spent Liquor Concentration, % solids	Combustion Temperature, °F.	
	Adiabatic, no heat loss	Heat Loss, (1 B.t.u./°F.)/lb. organic
20	828	706
25	1220	1019
30	1543	1269
35	1818	1476
40	2054	1650
45	2261	1797
50	2446	1925
55	2611	2037
60	2760	2137
65	2896	2225

The final item regarding the combustion of holopulp spent liquor is the type of furnace which would be used. This will depend primarily on the combustion temperature; in fact, the combustion temperature range that would be picked could well be determined by the availability of equipment.

It is possible that a somewhat modified version of present-day kraft recovery furnaces could be used. This would be a fully water-walled furnace for higher temperature operation with withdrawal of the recovered chemicals as molten smelt. Concentration of the incoming spent liquor would have to be quite high, possibly around 60% solids. It is conceivable that a direct-contact evaporator might be used to bring the liquor to firing concentration. It would be necessary to have provisions for handling the volatility of the NaCl, such as through soot

blowing. Kraft mills operating with salt-water-borne wood would have experience in solving this problem, although salt loadings would be much higher in holopulping.

There are several advantages to using this type of furnace for holopulp liquor combustion. This type of equipment exists, is known to work, and the pulp industry is quite familiar with its operation. Combustion stability should be quite good, and it would be quite efficient from an energy recovery standpoint. There are also some pronounced disadvantages. The capital costs of a unit of this type are very high. Operation at high temperature with attendant salt volatility problems is required. Concentrations of spent liquors are high, requiring a greater evaporator load. These units would have the same degree of proneness to smelt-water explosions as do kraft recovery furnaces, as well as greater potential HCl loss out of the stack.

An alternative means would be to use a fluidized-bed combustion process operating at temperatures below the melting point of the salts. It would appear that such a process would be predicated on the ability of Na_2CO_3 and NaCl to form particles of the proper characteristics to permit fluidized-bed operation since it is doubtful that an inert-bed material could be used without seriously interfering with the recovery of the NaCl and Na_2CO_3 formed in the furnace. It remains to be established that NaCl and Na_2CO_3 would have the proper characteristics. If they do, then the fluidized approach looks very promising. Fluidized-bed combustion would permit good temperature control and uniformity and would promote intimate contact of the gases with the solids. This should favor reduced chlorine compound emissions in addition to the effect of reduced temperature. Weak spent liquor could be sprayed into the bed, and solid NaCl and Na_2CO_3 withdrawn for further processing. A waste heat boiler could be used to extract heat for steam generation from the combustion gases.

It appears that such a fluidized-bed system would be the most favorable if it works. It would greatly reduce evaporator and furnace capital cost, at the sacrifice of some energy recovery plus the cost of supplying compressed air to the bed. Operation should be easier, with reduced emissions and a more usable form of recovered salts.

A great deal more work is necessary before definite conclusions can be drawn and detailed configurations made up for the spent liquor processing. This is particularly true of combustion. At present, this step is the key unknown in the process.

CHLORINE-CAUSTIC SYSTEM

The sodium chloride and sodium carbonate recovered from the combustion operation are the starting point for the regeneration of the cooking chemicals. The pulping reagents for the pulping process as it is presently conceived are ClO_2, NaOH, NaOCl, and possibly Cl_2. These must be obtained from the mixture of Na_2CO_3 and NaCl. Since hypochlorite can be made by reacting Cl_2 with NaOH, the recovered sodium should be converted to caustic soda (NaOH). The recovered chloride should initially be converted to chlorine since Cl_2 can be used by itself, directly reacted with NaOH to form hypochlorite, and also as a raw material for manufacture of chlorine dioxide. It is convenient, then, to arbitrarily divide the regeneration system into two distinct parts, the first concerned with generation of chlorine and caustic from the recovered salts, and the second concerned with production of ClO_2 from chlorine. This portion of the report will be concerned with chlorine-caustic generation.

There are essentially two commercial methods for production of caustic soda, causticizing sodium carbonate with lime, and electrolysis of a sodium chloride

solution. The choice would be obvious if the recovered salts were either NaCl or Na_2CO_3 rather than a mixture. Since a mixture of the two would be obtained, the initial choice is whether or not to separate the carbonate from the chloride and treat them separately or to convert all of the carbonate to chloride and proceed from there. This choice would depend in part on the ease of achieving the separation and on the relative amounts of sodium choride and sodium carbonate in the recovered material. The latter can be determined from the pulping chemical requirements. Assuming chemical requirements of 9% ClO_2, 10% NaOH, and 3% NaOCl, the amount of NaCl and Na_2CO_3 for a ton of pulp assuming complete chemical recovery are 305 lb. of NaCl and 185 lb. of Na_2CO_3. Inclusion of sodium chloride which could be present in the hypochlorite and caustic solutions plus any sodium chloride which would be formed from the use of chlorine in pulping would further shift the balance toward sodium chloride. Hence sodium carbonate will be the minor component in the mixture. It cannot be completely eliminated (regardless of chemical requirements) since an excess of sodium over chlorine (on a mole basis) is necessary to get complete chlorine recovery.

The solubilities of sodium chloride and sodium carbonate are reasonably comparable, and their separation by crystallization techniques would be difficult. If the carbonate is to be causticized, the solution of Na_2CO_3 and NaCl would have to be causticized directly and the NaCl then removed from the NaOH-NaCl solution by evaporation. Disregarding the possible interference of a large amount of sodium chloride on the causticizing reaction, this procedure would necessitate a lime cycle, including kiln, slaker, etc., and still would leave the bulk of the recovered material (NaCl) to be treated by other means. This approach does not appear very feasible, and it has been dropped from consideration for the present.

Thus, the regeneration of chemicals proceeds by converting the NaCl-$NaCO_3$ mixture to pure NaCl for electrolytic production of chlorine and caustic. This

conversion can be carried out quite simply by adding hydrochloric acid to the chloride-carbonate solution according to the reaction

$$Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2O + CO_2 .$$

The necessary hydrochloric acid can be obtained by reacting some of the chlorine and hydrogen obtained from the electrolytic cells according to the reaction

$$H_2 + Cl_2 \rightarrow 2HCl .$$

The inclusion of this loop in the process to convert all of the recovered material to sodium chloride makes complete electrolytic regeneration possible.

There are two common methods of electrolytic chlorine-caustic production. These are the use of diaphragm cells and the use of mercury cells. It appears that either of these methods could be adapted for use in the holopulping process. A good deal of careful evaluation would be required before selecting one approach for use in holopulping. Accordingly, each will be discussed below. The subsidiary operations of brine purification and internal recycles are sufficiently different from these two approaches so as to require each to be considered separately.

Diaphragm Cells

In a diaphragm cell, the anode and cathode are separated by a permeable diaphragm normally of deposited asbestos. Nearly saturated brine is fed into the anode compartment where chlorine is formed, then flows through the diaphragm into the cathode compartment where hydrogen and alkali are formed. The cell liquor leaving the cathode compartment contains both caustic and unelectrolyzed salt. The relative amounts of these two species, as quantified in the salt-caustic ratio, is an important operating parameter in diaphragm cell technology.

Generation of chlorine and caustic in diaphragm cells is a highly advanced art. Holopulping could confidently draw on a well-developed technology for the necessary cells. Accordingly, this discussion will not be concerned with details of cell design and operation per se. Rather, it will be directed primarily toward the integration of the diaphragm cell technology with the particular needs of the holopulping process. Specifically, this will be directed toward brine preparation aspects and means of handling and recycling the cell products. These derive from the requirements of the diaphragm cell.

The diaphragm cell requires a nearly saturated brine substantially free of impurities. It puts out a solution of salt and caustic soda. This cell liquor is then evaporated to precipitate NaCl (which is less soluble than NaOH) to provide the desired NaOH concentration and purity. The system is essentially open with respect to water. Water leaves the system with the caustic solution and as evaporator condensate. The major elements of a chlorine-caustic system based on diaphragm cells are a means of dissolving the recovered NaCl and Na_2CO_3 without overdilution, a means for purging the impurities from the system, a means for converting the carbonate to brine, provisions for adding the recycled salt from the caustic evaporator, the diaphragm cell itself, and the caustic evaporator. A schematic diagram for such a system is shown in Fig. 5.

The major impurities which would affect the operation of a diaphragm cell are Ca^{++} and Mg^{++} cations and the $SO_4^{=}$ anion. Presence of significant amounts of calcium and magnesium ions will cause the diaphragm to plug because the insoluble hydroxides $Ca(OH)_2$ and $Mg(OH)_2$ will precipitate in the diaphragm itself (due to the pronounced change in pH across the diaphragm). Any other metal ion which forms as insoluble hydroxide could lead to diaphragm plugging difficulties. If the sulfate concentration is too high, the efficiency of the electrolytic cell is decreased and the tendency to foul the caustic evaporators is increased.

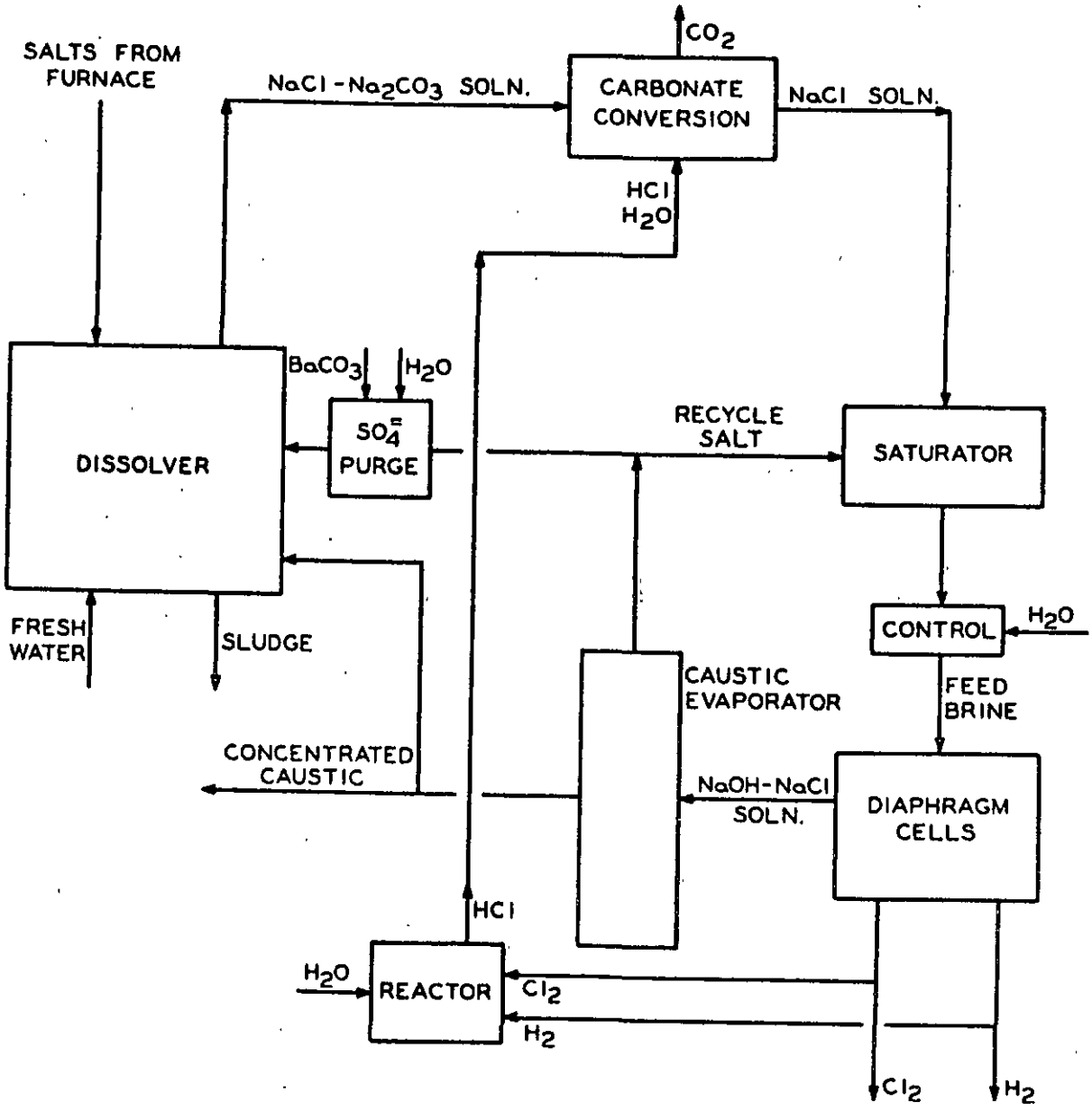


Figure 5. Schematic Diagram for a Diaphragm Cell System

Knowing the impurities which cause troubles in diaphragm cell operation, it is advantageous to consider the possible sources of impurities in the holopulping process. The major process inputs will be wood and water. It is expected that a certain amount of calcium will enter with the wood. Magnesium addition from this source should not be as significant. It is likely that the prime source of sulfate ions will be from the fresh water added to the system. Although careful barking of the wood and treatment of incoming water could minimize the addition rates of these impurities, the closed recyclic nature of the holopulp process will inevitably lead to a build-up of these materials. Thus, a purge stream is needed, and it appears more advisable to concentrate on effective purging rather than on minimizing impurity addition.

One conventional method of purifying brines involves a sequence of additions of $BaCO_3$, Na_2CO_3, and NaOH to knock out the sulfate, calcium, and magnesium, respectively. The relevant reactions are:

$$SO_4^{=} + BaCO_3 \rightarrow BaSO_{4\downarrow} + CO_3^{=}$$

$$Ca^{++} + Na_2CO_3 \rightarrow CaCO_{3\downarrow} + 2Na^{+}$$

$$Mg^{++} + 2NaOH \rightarrow Mg(OH)_{2\downarrow} + 2Na^{+} .$$

The sulfate is removed as barium sulfate, the calcium as calcium carbonate, and the magnesium as magnesium hydroxide. To a certain extent, these reactions can be utilized in the holopulping process. The material from the furnace consists mainly of NaCl and Na_2CO_3; hence a solution of NaCl and Na_2CO_3 is formed in the dissolver. The calcium present will be immediately knocked down as $CaCO_3$. If magnesium is present to a significant extent, some of the caustic solution from the cell can be added to precipitate it as the hydroxide. Removal of sulfate is a little more complicated. Direct addition of $BaCO_3$ to the dissolver would probably not be very effective. Barium carbonate is only about one order of magnitude more soluble than barium sulfate. Since a relatively large amount of carbonate would be present in the solution, the solubility of barium carbonate could be depressed to

the point where it would not be effective in removing the sulfate. Sulfate removal would have to be carried out elsewhere in the system.

Examination of Fig. 5 shows a closed loop involving the recycled salt from the caustic evaporator, the saturator, and the cell itself. It is in this loop that the sulfate concentration will build up to its highest level since the sodium sulfate will tend to drop out with the sodium chloride in the caustic evaporator. It appears that this recycled salt loop would be the best place to locate the sulfate purge. A portion of the recycled salt (the amount depending on the tolerable sulfate concentration) would be removed, dissolved in water, and treated with $BaCO_3$ to precipitate $BaSO_4$. The clarified liquor could then be sent to the dissolver where any remaining barium would be dropped as the carbonate.

It can be seen that methods of brine purification for the recovered solids from the furnace are available, and that a relatively simple process based on diaphragm cells can be used. Some typical material balance data for such a system are shown in Table IX. The purpose of these calculations is to show the expected magnitude of materials being processed, the amounts of impurities which may enter, and the chemical requirements for removing them, and to demonstrate the feasibility of the system.

It may be noted that fresh water is added at the dissolver, where the impurities are to be precipitated. Sufficient water must be added here so that all of the NaCl and Na_2CO_3 are solubilized, else they will be lost with the impurities. More water is added at the converter with the aqueous HCl solution, so that the brine stream leaving the converter should be significantly below saturation. It is necessary to bring the brine concentration close to saturation before entering the cell. The recycled salt from the caustic evaporator is used to achieve this. The amount of recycle salt available for saturating the brine is dependent on the

TABLE IX

MATERIAL BALANCE DATA FOR DIAPHRAGM CELL SYSTEM

Part I. Basis of Calculation

Pulping Conditions

Basis: One ton pulp at 67% yield

Chemical Usage: ClO_2, 9% of original wood
NaOH, 10% of original wood
NaOCl, 3% of original wood (from Cl_2 and NaOH)

Water Usage: Pulp exit consistency = 20%
Washing dilution factor = 3

Assumed Impurities

Water Supply: Ca^{++} = 200 p.p.m.
Mg^{++} = 100 p.p.m.
$SO_4^{=}$ = 100 p.p.m.

Wood Supply: 0.3% ash as $CaCO_3$

Cell System Parameters

Brine entering cell: 0.35 lb. NaCl/lb. H_2O, density = 1.2 g./cc.

Cell effluent: Salt-caustic ratio = 1.4

Maximum allowed sulfate concentration in cell: 5 g./liter as Na_2SO_4

Final caustic concentration: 50% by weight (salt-caustic ratio = 0.06)

Available HCl concentration: 20% HCl by weight

Moisture content of recycled salt: 1 lb. H_2O/lb. NaCl.

It is assumed that no sulfate leaves with the caustic.

TABLE IX (Contd.)

MATERIAL BALANCE DATA FOR DIAPHRAGM CELL SYSTEM

Part II. Basis of Calculation

At dissolver		lb.	
Entering from furnace	NaCl	400	
	Na_2CO_3	180	
	$SO_4^=$	1.4	
	Ca^{++}	6.4	
	Mg^{++}	1.4	
Treated recycle salt	NaCl	110	
	H_2O	320	
	$BaCO_3$	3.5	
NaOH to precipitate Mg^{++}	NaOH	6	
Fresh water make-up	H_2O	2000	
	$SO_4^=$	0.2	
	Ca^{++}	0.4	
	Mg^{++}	0.2	
To precipitate Ca^{++}	Na_2CO_3	17	(180 lb. available)
Concns. leaving dissolver	NaCl	0.22/lb. H_2O	
	Na_2CO_3	0.077/lb. H_2O	

(These are safely below solubility limits.)

TABLE IX (Contd.)

MATERIAL BALANCE DATA FOR DIAPHRAGM CELL SYSTEM

		lb.
At converter		
Additions	HCl	125
	H_2O	500
Exit stream	NaCl	710
(0.25 lb. NaCl/lb. H_2O, which is soluble)	H_2O	2820
At saturator		
Additions	recycled salt	420
	H_2O	420
Exit stream	NaCl	1130, at 0.35 lb./lb. H_2O
At diaphragm cell		
Exit stream	NaOH	395
	NaCl	550
	Cl_2	350
	H_2	10
At evaporator		
Concentrated caustic	NaOH	395
	NaCl	20
	H_2O	395
Recycled salt	NaCl	530
	H_2O	530
Water evaporated		~ 1500

Note that about 20% of the recycled salt must be treated with $BaCO_3$ in order to limit the Na_2SO_4 concentration in the cell to 5 g./liter.

degree of concentration of the caustic and on the amount of recycle salt which must be treated to purge sulfate from the system. This affects the freedom to carry out the caustic evaporation to any degree desired since a certain minimum amount of recycle salt must be provided.

For the conditions chosen for the calculations in Table IX, it appears that the system will perform satisfactorily. Adequate carbonate to drop out the calcium is available, and relatively small amounts of NaOH and $BaCO_3$ are needed to drop out the magnesium and sulfate. It is felt that the values chosen for impurity addition rates were somewhat on the high side, so that these represent a sort of "worst case." Solubility requirements in the dissolver and converter are also met and there is no difficulty in achieving a saturated brine at the cell inlet.

These values would be changed somewhat if the caustic concentration is carried out to less than 50% caustic since less salt would be dropped out of the caustic-salt solution. Fortunately, the bulk of the salt drops out in the early part of the evaporation. At a final caustic concentration of 30%, the amount of salt leaving with the caustic is four times greater than with 50% caustic. In this case, about 80 lb. of salt would leave with the caustic, and the recycle salt would be reduced to about 460 lb. This is still sufficient for the process shown in Fig. 5 to work. However, the amount of recycled salt would fall rapidly as the caustic concentration falls below 30%, so that it appears that a caustic concentration of about 30% is the minimum feasible concentration with this system.

It may be noted that the system shown in Fig. 5 and discussed above does <u>not</u> provide for the purge of Ca^{++} and Mg^{++} entering with the HCl solution before the brine reaches the cell. The amounts of impurities added here may be small enough to cause no problems; however, a potential problem is present. If difficulty from this source is encountered, several alternatives are available for

mitigating the problem. The water used to absorb HCl gas could be treated to remove magnesium and calcium ions. Another method would be to use condensate from the caustic evaporator for the water supply to absorb the HCl since it would be substantially free of these impurities. Alternatively, the conversion could be carried out with gaseous HCl.

In summary, it appears that a chlorine-caustic system based on diaphragm cells is workable. Means of purging materials which interfere with diaphragm cell performance are readily available. Water balance problems in the diaphragm cell system do not appear to be too severe. If water balance problems do occur, it is possible that the conversion of carbonate to chloride could be carried out with gaseous HCl or, in an extreme, an additional evaporator could be used to concentrate the brine before it arrives at the cell.

Mercury Cells

Mercury cells derive their name from the use of a flowing mercury cathode. No diaphragm separates the anode from the cathode in a mercury cell. The mercury cell consists of two essential parts: an electrolyzer and a decomposer. In the electrolyzer, saturated brine is subjected to electrolysis. Chlorine gas is given off at the anode and sodium metal is deposited at the surface of the mercury cathode, in which it dissolves to form a liquid amalgam. In the decomposer, the sodium in the amalgam is reacted with water to form caustic and hydrogen. The basic chemical reactions can be written as follows.

In the electrolyzer: $NaCl + (hg) \xrightarrow{1\ \text{faraday}} Na(Hg) + \frac{1}{2}Cl_2$.

In the decomposer: $Na(Hg) + H_2O \xrightarrow{1\ \text{faraday}} NaOH + \frac{1}{2}H_2 + (Hg)$.

Overall: $NaCl + H_2O \xrightarrow{1\ \text{faraday}} NaOH + \frac{1}{2}H_2 + \frac{1}{2}Cl_2$.

It can be seen that the mercury serves as a carrier and does not take part in the overall reaction. A closed circulation of the mercury through electrolyzer and decomposer is maintained by means of a pump or other device. A major feature of this cell is that there is no direct connection between the brine in the electrolyzer and the caustic solution in the decomposer. For this reason, the caustic produced in a mercury cell is essentially free of NaCl contamination and can be easily obtained directly at high concentrations (e.g., 50% caustic), thus eliminating the need for a caustic evaporator.

The unique feature of the mercury cell is that the gases produced, chlorine and hydrogen, are released in two spatially separated compartments and the caustic production occurs apart from the brine. This occurs because the hydrogen overvoltage on the mercury cathode is sufficiently high so that deposition of metallic sodium and its resultant amalgamation occurs instead. Any factor which lowers the hydrogen overvoltage causes problems in the mercury cell. Contamination with heavy metals is of great concern in mercury cells since they lower the overvoltage of hydrogen. As this occurs, hydrogen is produced at the cathode, contaminating the chlorine, forming caustic in the brine, and reducing caustic production in the decomposer. Substantially complete removal of heavy metals such as iron, nickel, vanadium, chromium, and molybdenum from the brine is required since they all lead to hydrogen evolution at the cathode.

The basic characteristics of the mercury cell require a system which is significantly different from the diaphragm cell system. Brine purity requirements are somewhat more stringent. In addition, only about 15% of the NaCl is electrolyzed in a given pass through the cell, and the unelectrolyzed brine is recirculated. Mercury cell systems normally employ solid salt to resaturate the recirculating brine since there is no direct aqueous outflow from the brine side of the system.

In essence, the mercury cell system is closed loop with regard to water, while the diaphragm cell system is basically open loop.

A schematic diagram for a chlorine-caustic system employing mercury cells which is adaptable to holopulping conditions is shown in Fig. 6. The system consists of a dissolver, a converter, a concentrator, the mercury cell, and a dechlorinator. The sulfate purge is located ahead of the dissolver in order to avoid problems of low $BaCO_3$ solubility at the carbonate concentrations which exist in the dissolver. The concentrator (or evaporator) is present to permit achieving a saturated brine feed to the cell.

The possible need of a concentrator shows the severity of the water balance problem in the brine loop. Water would be removed from this system only as water vapor along with the chlorine from the electrolyzer and dechlorinator, and with the sludge from the dissolver. Water will enter at the carbonate converter (some is even formed by the reaction) and could enter with the recovered salt from the furnace depending on recovery practice. Entering and leaving water must be balanced. An additional complexity arises from the fact that the conversion to carbonate adds water <u>after</u> the dissolver. Thus, even if the solution leaving the dissolver is saturated, the brine will be diluted below saturation in the dissolver.

There appear to be three methods of achieving a saturated brine feed to the electrolyzer under these circumstances. The first is to use a brine evaporator (concentrator) to remove water from the brine prior to the cell. This is the system shown in Fig. 6. The second method would be to use gaseous HCl directly in the converter and avoid dilution at this point. A third would be to recycle a portion of the brine leaving the converter back to the dissolver, so that the slightly greater solubility of sodium carbonate over sodium chloride would permit

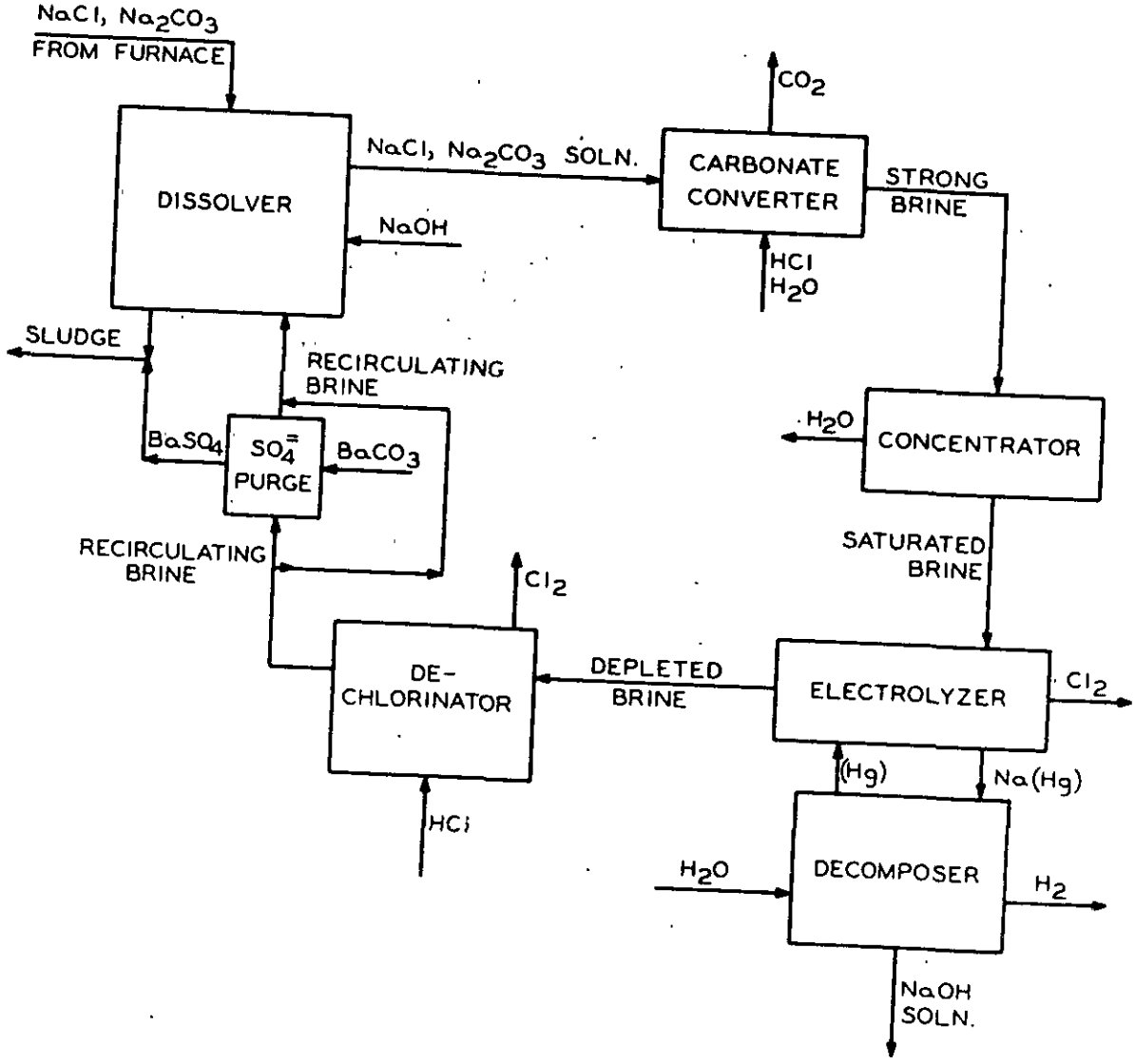


Figure 6. Schematic Diagram for a Mercury Cell System

saturation at both the dissolver and the converter. This would require a relatively large recycle stream.

The latter two methods are limited to the situation where the incoming water is entering with aqueous HCl at the converter. If water also enters the system at other locations, only the method shown in Fig. 6 would be effective. It appears possible that some water will enter with the material recovered from the furnace. It is unlikely that the hot solids from the furnace would be added directly to the absorber. They might be quenched with water for cooling and transport purposes. In this case, only the first method would be successful.

Material balance data for the system shown in Fig. 6 are presented in Table X. These data illustrate the kinds of values which might be obtained. The tightness of the water balance is clearly shown. Only a small amount of water is removed from the system at the electrolyzer and the dechlorinator. The concentrator is needed. Comparing these values with those for the diaphragm cell system in Table IX, it is seen that much more material flows and recirculates in the mercury cell system. The rate of brine flow to the mercury cell is more than three times as great as for the diaphragm cell. Recirculation is enormous. The amounts of water added and removed from the system are small fractions of the total water flowing in the system. This has a bearing on the water balance. The concentrator removes about one fourth as much water as the caustic evaporator in the diaphragm cell system, but if incoming solids are sluiced, evaporator requirements become comparable.

TABLE X

MATERIAL BALANCE DATA FOR MERCURY CELL SYSTEM

Part I. Basis of Calculation

Pulping Conditions

Basis:	One ton pulp at 67% yield	
Chemical usage, % of original wood:	ClO_2, %	9
	NaOH, %	10
	NaOCl (from Cl_2 and NaOH), %	3
Water usage:	Pulp exit consistency, %	20
	Washing dilution factor	3

Assumed Impurities

Water supply, p.p.m.:	Ca^{++}	200
	Mg^{++}	100
	$SO_4^{=}$	100
Wood supply:	0.3% ash as $CaCO_3$	

Cell System Parameters

Brine entering cell, lb. NaCl/lb. H_2O:	0.35
Density, g./cc.:	1.2
Conversion per pass, % of salt reaching cell:	15
Cell effluent, g./liter dissolved chlorine:	0.5
Cell temperature, °F.:	180
Final caustic concn., % by weight NaOH	50
Available HCl concn., % by weight HCl:	20

Water losses at electrolyzer and dechlorinator estimated from vapor pressures.

TABLE X (Contd.)

MATERIAL BALANCE DATA FOR MERCURY CELL SYSTEM

Part II. Results of Calculations

At Dissolver		
Entering from furnace:	NaCl, lb.	400
	Na_2CO_3, lb.	180
	$SO_4^{=}$, lb.	1.4
	Ca^{++}, lb.	6.4
	Mg^{++}, lb.	1.4
Recirculating brine:	NaCl, lb.	3400
	H_2O, lb.	11,300
NaOH to precipitate Mg^{++}:	NaOH, lb.	5
$BaCO_3$ to drop $SO_4^{=}$:	$BaCO_3$, lb.	3
Na_2CO_3 to drop Ca^{++} (180 lb. available)	Na_2CO_3, lb.	17
Concns. leaving dissolver: (Joint solubility at these concns. is marginal.)	NaCl, lb./lb. H_2O	0.336
	Na_2CO_3, lb./lb. H_2O	0.016
At Converter		
Additions:	HCl, lb.	125
	H_2O, lb.	500
Exit stream:	NaCl, lb.	4000
	H_2O, lb.	11,800
At Concentrator		
Water evaporated, lb.:		400
Exit stream, at 0.35 lb. NaCl/lb. H_2O:	NaCl, lb.	4000

TABLE X (Contd.)

MATERIAL BALANCE DATA FOR MERCURY CELL SYSTEM

At Electrolyzer		
Exit streams:	Chlorine, lb.	360
	Water vapor, lb.	75
	NaCl, lb.	3400
	H_2O, lb.	11,325
	Dissolved chlorine, lb.	6
At Dechlorinator		
Exit streams:	Chlorine, lb.	6
	Water vapor, lb.	25
	NaCl, lb.	3400
	H_2O, lb.	11,300
At Decomposer		
Additions:	H_2O, lb.	500
Exit streams:	NaOH, lb.	410
	H_2O, lb.	410
	H_2, lb.	10

The need for high recirculation, closed-loop operation of the mercury cell system stems from the processes occurring in the cell itself. As electrolysis proceeds in the mercury cell, sodium and chloride ions are removed from the solution and are not replaced by other ions. This not only increases the resistance of the electrolyte (which increases the power needed) but also makes undesirable cell reactions more likely. Accordingly, the conversion per pass is limited and recirculation is needed.

There are three major reasons for dechlorinating the recirculating brine. They are:

1. It is difficult to control iron removal in the presence of hypochlorite ion.
2. If hypochlorous acid is not removed, the chlorate content of the brine will build up to the point where graphite consumption is adversely affected.
3. Brine resaturation is less complicated and less nauseous if the brine contains no free chlorine.

Brine dechlorination proceeds in two steps. The brine is acidified with HCl to convert any hypochlorous acid to chlorine according to the reaction

$$HCl + HOCl \rightarrow Cl_2 + H_2O \ .$$

The chlorine is then stripped from the brine. If hypochlorite solution is needed (as in the holopulp process), stripping can be carried out by blowing the brine with air in a packed tower. The chlorine can then be scrubbed from the air with a dilute caustic solution to form hypochlorite.

It has been mentioned previously that heavy metal impurities such as iron, nickel, vanadium, chromium, titanium, and tantalum cause difficulty. It may be noted that the system diagram, Fig. 6, does not show means for eliminating these impurities. Heavy metals are usually sufficiently absorbed by the other precipitates formed; if not, the brine is deliberately treated with calcium and iron to increase the precipitate volume until control is obtained. Hence, the heavy metals are removed along with the calcium, magnesium, and sulfate. The best means of controlling heavy metals would be to prevent them from entering the system. This may be difficult in holopulping since it uses some corrosive chemicals. The heavy metals listed are the same ones which are used in making corrosion-resistant metals. Thus, it is likely that heavy metal contaminants from corrosion products will show up in the furnace solids.

Comparison of Cell Types

The advantages and disadvantages of diaphragm cells and mercury cells and their associated systems must be considered in order to ultimately select the best system for the holopulping process. In this connection, it should be pointed out that the major advantage of the mercury cell, producing a pure, concentrated caustic solution, does not appear to be a significant advantage in holopulping. A listing of the advantages and disadvantages of each type is presented in Table XI.

The complexity of the two systems appears to be comparable. The mercury cell itself would seem to be somewhat more complicated than the diaphragm cell. On the other hand, a caustic evaporator is a necessity with the diaphragm cell. This is counterbalanced to some extent by the need for a dechlorinator and concentrator in the mercury cell system.

TABLE XI

MERCURY CELLS VERSUS DIAPHRAGM CELLS

Mercury Cells	Diaphragm Cells
Advantages	
1. Produce a pure, concentrated caustic solution without needing a caustic evaporator.	1. Require about 15% less power than mercury cells.
2. Require fewer cells for the same production tonnages.	2. Require less floor space (order of one half) than do mercury cells for the same production tonnages.
3. Chlorine and hydrogen contain less water vapor because cell operating temperatures are lower.	3. Installation costs are slightly lower than for mercury cells.
4. Anode lifetimes are comparable with diaphragm cells, but there are no diaphragms to be replaced (which require shutdown).	4. Brine purity requirements are not as severe since heavy metal contamination does not affect cell performance to the same degree as in mercury cells.
Disadvantages	
1. A large mercury inventory is needed. This is not only a large, nondepreciating capital expense, but also involves a pollution hazard due to the inevitable losses of mercury.	1. The cell liquor contains more sodium chloride than caustic. It is necessary to evaporate this cell liquor to concentrate the caustic and remove the unelectrolyzed salt. This is a somewhat messy operation.
2. Some hydrogen will be present in the chlorine, becoming excessive if brine purity gets out of control. Precautions must be taken to ensure that the concentrations of hydrogen in the chlorine do not get into a hazardous region.	2. From two to three diaphragms are normally required during the lifetime of an anode. This causes an operating cost due to the asbestos needed, the labor required to replace the diaphragms, and lost production time.
3. The hydrogen gas from the decomposer will contain some mercury vapor. This would have to be condensed and removed.	3. Due to high cell temperatures, the chlorine and hydrogen are obtained quite wet (have a good deal of water vapor present). Depending on use, it may be necessary to remove this water vapor in additional processing steps.

TABLE XI (Contd.)

MERCURY CELLS VERSUS DIAPHRAGM CELLS

Mercury Cells	Diaphragm Cells
4. Care would have to be taken to ensure that caustic solution is free of mercury since any mercury in the caustic would eventually reach the furnace.	4. There may be mechanical problems in obtaining, transporting, and otherwise handling the recycle salt from the caustic evaporator.
5. The water balance problem could make this system difficult to control without the use of a brine evaporator.	5. The procedure for removing sulfate is slightly more complicated in the diaphragm cell system.
6. High recirculation rates in the in the mercury cell system would probably require larger tanks for dissolution, carbonate conversion, and brine storage.	6. More fresh water is added in the diaphragm cell system. This may require larger water treatment facilities.
7. The decomposers require a supply of soft water. Hence, this water must be treated.	

On balance, it would appear that most of the advantages of the mercury cell are not that important in the holopulping process. There appears to be no real need for high-purity caustic since the salt carried with the caustic will eventually return to the furnace and hence recirculate. High-purity caustic would be required only if the presence of significant amounts of sodium chloride would have a deleterious effect on the alkaline extraction operation in the pulping sequence. This remains to be determined. It also appears likely that wet cell gases could be used directly in the process, although the water could be removed relatively easily since liquid chlorine is not needed. At present, it appears that, all other factors being equal, the potential pollution problems associated with having mercury in the system would favor the use of diaphragm cells.

In summary, processes using either diaphragm or mercury cells are feasible in a holopulping chemical recovery system. Chlor-alkali production based on either type of cell is well advanced technologically. Thus, it is felt that this part of the system is least critical to the success or failure of the holopulping process. Development work on this aspect of the process is not expected to be major. At the present time, it appears that the system based on the use of diaphragm cells is more appropriate to this holopulping process. However, no definite commitment to this particular route has been made.

HYPOCHLORITE PRODUCTION

Hypochlorite needed is easily produced by reacting chlorine gas with caustic solution according to the reaction:

$$Cl_2 + 2NaOH \rightarrow NaOCl + NaCl + H_2O \ .$$

Each of these reactants is produced by the chlor-alkali cells so that all that is needed for hypochlorite production is to carry out the reaction. Commercial

systems are available (e.g., Hooker's sodium bleach liquor system) for carrying out this reaction under controlled conditions. The use of hypochlorite in the holopulping process has another advantage. Chlorine gas effluent streams (as for example from a brine dechlorinator) can be absorbed in dilute caustic solutions to supplement the hypochlorite supply. This helps eliminate potential air pollution problems.

HYDROCHLORIC ACID PRODUCTION

In the holopulp recovery process a significant amount of hydrochloric acid is required to convert the sodium carbonate to sodium chloride. The hydrochloric acid needed is obtained by reacting some of the hydrogen and chlorine from the electrolytic cells. Formation of hydrogen chloride according to the reaction

$$H_2 + Cl_2 \rightarrow 2HCl$$

rests on well-established technology. The hydrogen chloride is produced by combustion of a controlled mixture of hydrogen and chlorine gas. Normally, hydrogen is supplied in a slight excess (2-5%) over stoichiometric to ensure a chlorine-free product. The hydrogen and chlorine may be wet or dried.

The essential parts of an apparatus to carry this out are: a burner and combustion chamber, control and safety devices, and facilities for processing the product hydrogen chloride.

The burner is a nozzle that injects reactants into the combustion space. Combustion chambers may be made of silica, brick-lined steel, water-jacketed steel, or water-cooled graphite. Silica is limited to small units. Brick-lined steel combustion chambers have been used in large units, but product gas temperatures may reach 2200°F. and higher. Water-jacketed steel must be kept above the dew point

of the gases to minimize corrosion; even so, there will be a trace of ferric chloride in the product. Graphite is an excellent material for burning wet or dry gases. Exit gas temperatures of a water-cooled graphite combustion chamber run from 400 to 600°F.

A retractable torch with an air-hydrogen flame is commonly used to ignite the hydrogen at the burner tip. Chlorine is then passed into the burner to establish a hydrogen-chlorine flame. Controls must include safety devices because chlorine and hydrogen can form explosive mixtures. The combustion chamber normally contains a safety explosion disk. A combustion controller actuated by a photoconductive eye closes both hydrogen and chlorine valves if there is a flame failure. A flame arrester is placed in the hydrogen feed line to prevent propagation of flameback into the supply line. The combustion system is normally purged with air or inert gas after interruption of service.

The hydrogen chloride produced by combustion may be used directly or absorbed in water to make hydrochloric acid. The presence of water vapor in reactants and products is not objectionable if hydrochloric acid is the desired product. It is expected that hydrochloric acid would be used for conversion of carbonate to chloride since it would permit a simple stirred-tank reactor to be used. In addition, storage as hydrochloric acid would be much simpler than storage of gaseous hydrogen chloride. Gaseous hydrogen chloride for carbonate conversion would be considered only if the mercury cell system were chosen.

In some of the processes for generating chlorine dioxide, notably the Chemech process, hydrogen chloride is formed by burning hydrogen and chlorine. In this case, some of the HCl so produced could be used for carbonate conversion in the chlorine-caustic system. This would avoid the use of two separate combustion systems.

CHLORINE DIOXIDE PRODUCTION

The final subsystem in the holopulping process is concerned with the generation of chlorine dioxide for use in the oxidation stages of the pulping process. Since the advent of chlorine dioxide bleaching on an industrial scale, many commercial processes for producing chlorine dioxide have come into existence. All of them are based on the reduction of chlorate in a strongly acid medium. They differ mainly in the reducing agent which is used. At the present stage of development of the holopulping process, it does not appear advantageous to attempt to develop new methods of producing chlorine dioxide. Instead, reliance has been placed on existing chlorine dioxide technology, and effort has been devoted to selecting that process which is most readily adapted to holopulping and integrating it into the holopulping system.

Nearly all of the major commercial ClO_2 processes employ a very concentrated sulfuric acid solution as the substrate for carrying out the reduction of chlorate. The dominant characteristics of these processes are shown in Table XII.

Several features of these processes are very important from the holopulping standpoint. All of them have sodium sulfate as a by-product, while three of them have sodium sulfate in a highly acidic sulfuric acid solution. These by-products are not a problem in kraft bleaching since the generator effluents can be used to acidulate tall oil and as a substitute for make-up salt cake in the recovery furnace. In the holopulping process, they constitute a disposal problem since there is no direct, inherent use for them. It is conceivable that these processes could be used for ClO_2 generation if the holopulping process were operated as an adjunct to a kraft process. However, holopulp production would be limited to a small fraction of the kraft production since the ClO_2 requirement for

holopulping is relatively high (compared with bleaching requirements) and the attendant load of sulfuric acid and sodium sulfate would have to be borne by the kraft system.

TABLE XII

CHARACTERISTICS OF SULFURIC ACID-BASED ClO_2 PROCESSES

Process	Reductant	Inputs	Outputs	
Mathieson	SO_2	$NaClO_3$	ClO_3	gas
		H_2SO_4	H_2SO_4	solution
		SO_2	Na_2SO_4	
Solvay	methanol	$NaClO_3$	ClO_2	gas
		H_2SO_4	H_2SO_4	solution
		methanol	Na_2SO_4	
R-2	NaCl	$NaClO_3$	ClO_2	gas
		NaCl	Cl_2	
		H_2SO_4	H_2SO_4	solution
			Na_2SO_4	
R-3 or SVP	NaCl	$NaClO_3$	ClO_2	gas
		NaCl	Cl_2	
		H_2SO_4 (less)	Na_2SO_4	crystal

There is another problem involved in integrating any of the processes in Table XII into the holopulping system. In all of these processes, the chlorine dioxide comes from the chlorate. If the reaction proceeds ideally, one mole of ClO_2 is formed for each mole of $NaClO_3$ which reacts. This means that for each mole of ClO_2 produced, one mole of sodium must take part, and this eventually shows up in

the generator effluent as sodium sulfate. The chlorate taking part in the reaction could either be purchased as such or be formed from sodium chloride in a chlorate cell. In any event, the sodium would eventually leave the system as sodium sulfate. This would prevent closure of the sodium and chlorine cycles over the holopulping process. As was discussed earlier in this report, the sodium and chlorine from the pulping steps are recovered at the furnace as NaCl and Na_2CO_3. All of the sodium which is present at this point derives from the chlor-alkali system (caustic extraction and hypochlorite pulping steps). The bulk of the chlorine, on the other hand, derives from the ClO_2 system (oxidation pulping step). These cannot be brought into balance if any of the processes listed in Table XII are used since they all purge sodium from the system as sodium sulfate.

This may perhaps be made clearer by considering some examples. Assume purchased sodium chlorate is used to operate the ClO_2 system. For each mole of $NaClO_3$ entering, a mole of chlorine and a mole of sodium enter. This sodium is removed from the system directly as Na_2SO_4, and to maintain a material balance an equivalent weight of chlorine must be removed from the system somewhere. It could be removed as chlorine gas from the chlor-alkali cells since that amount of chlorine corresponding to the ClO_2 would not be needed. Alternatively, purchased caustic soda could be added directly to the extraction step and the chlorine equivalent to the ClO_2 used removed as NaCl. It is clear that this picture would be changed if purchased NaCl were fed to a chlorate cell to form $NaClO_3$ for ClO_2 production by one of the above-mentioned processes.

The situation would not be changed to any extent if sodium chloride recovered from the furnace were fed to chlorate cells for the purpose of generating ClO_2. Sodium would still be purged as Na_2SO_4 in the ClO_2 generator effluent. In this case, the problem would show up as a shortage of NaCl at the chlor-alkali cells for caustic production. Again, it would be necessary to add sodium chloride

and remove the excess chlorine generated at the chlor-alkali cells, or supply purchased caustic soda to make up for the sodium loss.

The constraints of operating with any of the conventional sulfuric acid-based ClO_2 generation processes are thus obvious. First, it would be necessary to sell or otherwise dispose of a sodium sulfate-sulfuric acid solution (solid Na_2SO_4 if R-3 or SVP were used). It would also be necessary to either sell by-product chlorine or else purchase caustic soda to maintain a material balance. While these steps are not wholly impracticable, it is desirable to consider other methods of chlorine dioxide generation not based on sulfuric acid even though they have not met with commercial success in kraft bleaching systems.

It is obvious from the foregoing discussion that the source of the difficulties using the conventional processes is the sulfuric acid which is used since this introduces sulfate into the process. This difficulty would be eliminated if hydrochloric acid were used in place of sulfuric acid since the chemicals involved – $NaClO_3$, NaCl, and HCl – are all part of the chlor-alkali family. Processes based on the use of hydrochloric acid will now be considered.

The most promising processes for generating ClO_2 for holopulping are various versions of the Day-Kesting process. In this process, HCl serves as the acid medium and also as the agent for reducing the chlorate. The basic reaction can be represented stoichiometrically as

$$NaClO_3 + 2HCl = ClO_2 + \tfrac{1}{2}Cl_2 + NaCl + H_2O$$

with an undesired side reaction given by

$$NaClO_3 + 6HCl = 3Cl_2 + NaCl + 3H_2O .$$

It may be noted that the chlorine dioxide-producing reaction generates a half mole of chlorine gas for each mole of chlorine dioxide produced. This is characteristic of all chlorine dioxide generation processes in which chloride ion is the

reductant (for example, R-2 or R-3). If a chlorine-free chlorine dioxide is needed, further processing is necessary to separate the chlorine from the chlorine dioxide.

The sodium chlorate is converted to sodium chloride in the reaction. Since sodium chlorate is manufactured electrolytically from sodium chloride in chlorate cells, the reaction lends itself to the electrolytic regeneration of sodium chlorate from the sodium chloride produced by the reaction, and hence the possibility of closed recirculation of the sodium. This is the essence of the Day-Kesting process, which involves two major operations – the reaction of HCl with $NaClO_3$ to form ClO_2, and the recirculation of the generator effluent to chlorate cells for refortification of the chlorate content. A schematic diagram of the Day-Kesting process is shown in Fig. 7. Only a portion of the chlorate is reacted in a single pass through the generator.

The Day-Kesting process was operated commercially at Brown Company in Berlin, New Hampshire, and at least at four mills in Europe. The operation at Brown Company has been shut down, and the fate of the European operations is unknown to this author. The difficulties which led to the commercial abandonment of the process were due largely to mechanical, operational, and control problems rather than inherent in the process concept. In addition, the Day-Kesting process was competing with other processes for producing chlorine dioxide for bleaching kraft pulp, a situation wherein the by-products of the sulfuric acid-based processes did not cause problems, and actually acted as cost credits.

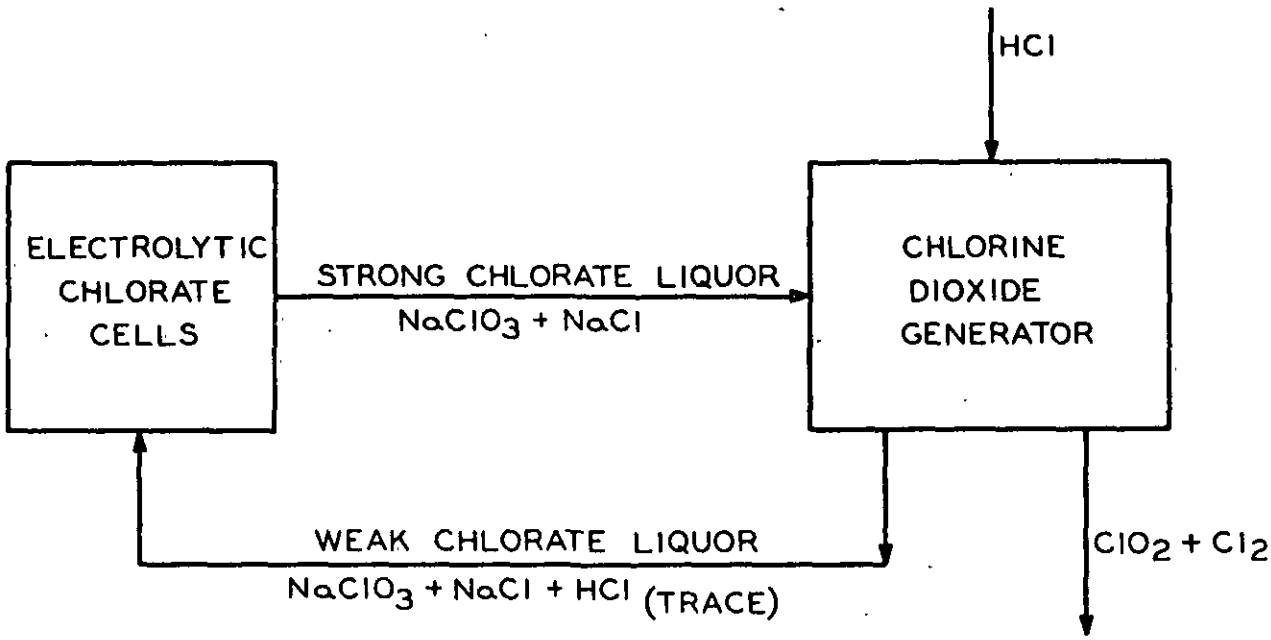


Figure 7. Schematic Diagram of Day-Kesting Process

Chemech Process

Recently a modified version of the Day-Kesting process was successfully piloted by Chemech Engineering Ltd. It appears that the difficulties of the old process have been largely overcome. A schematic diagram of the Chemech process is shown in Fig. 8. This is based on information obtained from Canadian patent 782,574.

The Chemech process uses chlorine gas as the raw chemical to produce chlorine dioxide without a liquid or solid effluent. Hydrogen is the only by-product. As illustrated in Fig. 8, sodium chloride-sodium chlorate solution recirculates between the chlorate cell and the ClO_2 generator, with the chlorate consumed in the generator refortified in the cell. Hydrogen gas evolved from the chlorate cell is reacted with chlorine to form hydrogen chloride. The HCl is sent to the generator where it reacts with the chlorate to form ClO_2 and Cl_2. These gases are separated by absorbing the ClO_2 in water, and the unabsorbed chlorine is recycled to the combustion chamber for further production of HCl. In the version of the process disclosed in Canadian patent 782,574, hydrogen gas is used as a diluent in the generator and is purged from the system at a scrubber (where hydrochloric acid is formed). The stoichiometric relations for the critical parts of this process are:

Cell: $NaCl + 3H_2O + 6 \text{ faradays} = NaClO_3 + 3H_2$

Combustion: $H_2 + Cl_2 = 2HCl$

Generator: $NaClO_3 + 2HCl = NaCl + ClO_2 + \frac{1}{2}Cl_2 + H_2O$

and the overall balance becomes:

Overall: $\frac{1}{2}Cl_2 + 2H_2O + 6 \text{ faradays} = ClO_2 + 2H_2$.

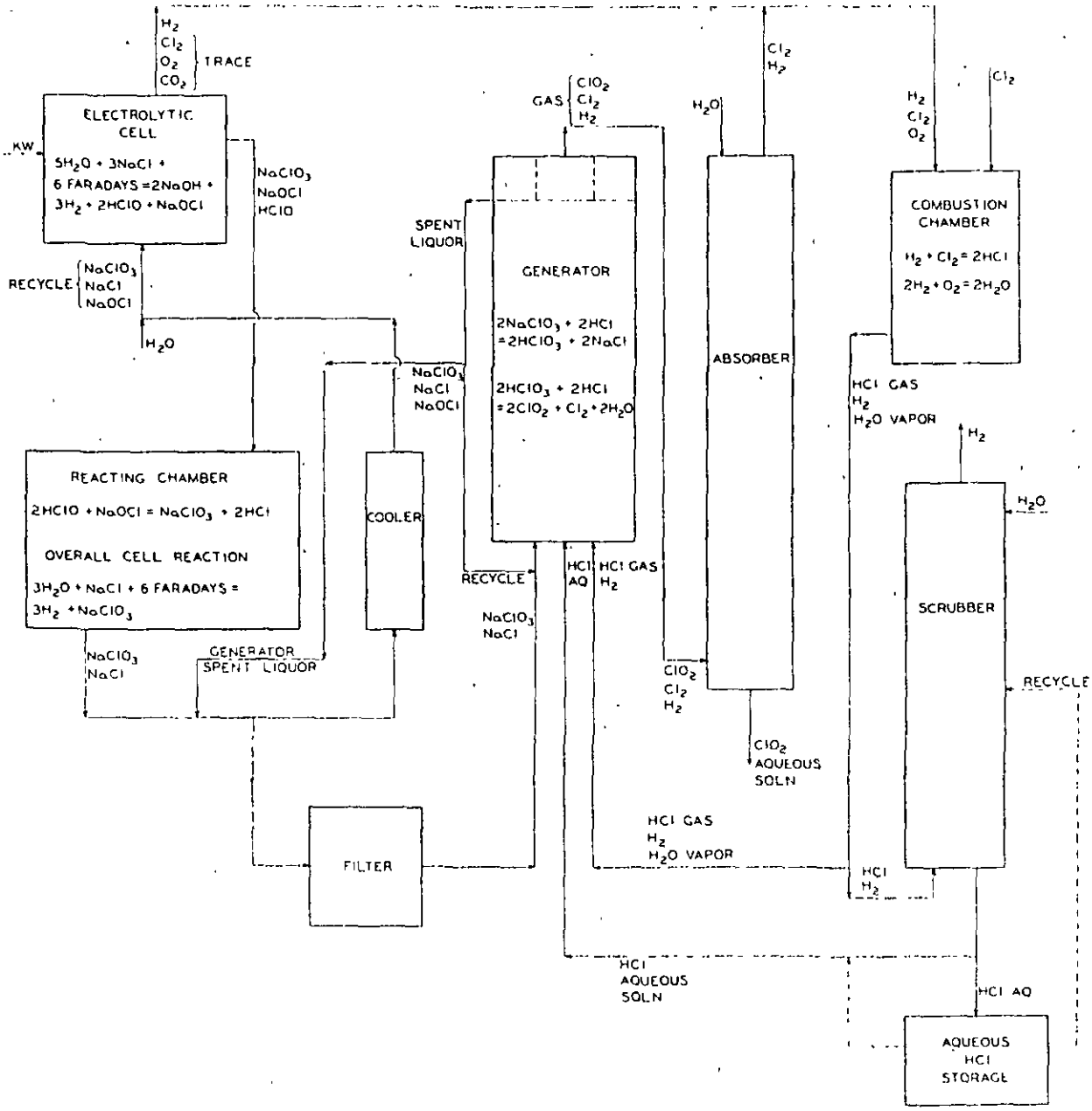


Figure 8. Schematic Diagram of Chemech Process

Thus, the Chemech process produces chlorine dioxide from chlorine; hydrogen gas is the only effluent.

The Chemech chlorate cell is of the bipolar type, using graphite electrodes as both anode and cathode. The electrodes are closely spaced in the cell, which is flooded with electrolyte to limit the gas space and to submerge the internal electrical connections. Chromate is added to prevent reduction of hypochlorite and chlorate ions to chloride at the cathode. An external degasifier is used to remove the hydrogen from the cell liquor. Formation of chlorate by the reaction

$$2HClO + OCl^- \rightarrow ClO_3^- + 2HCl$$

is completed in reaction tanks outside the cell. A good deal of recirculation of liquor is provided. Chemech chlorate cells have met with commercial success. The first industrial installation was placed in operation in late 1965 at Bellingham, Washington. Additional installations have taken place since then.

The chlorine dioxide generator is a packed column. The chlorate-rich feed is acidified with hydrochloric acid. This acidified liquor is brought into intimate contact with gaseous hydrogen chloride in the packed tower. This procedure is used to minimize chlorine production by the undesired reaction $NaClO_3 + 6HCl \rightarrow 3Cl_2 + NaCl + 3H_2O$. The efficiency of generation is highly dependent upon operating temperature, chlorate/chloride ratio, and control of acidity. Details of the pilot-plant operation have not been disclosed. It is believed that Chemech does know how to control the generator variables so as to obtain high efficiency.

The gas stream from the generator passes through an entrainment separator to the absorber where chlorine dioxide is separated from the chlorine.

Separation is achieved through the much greater solubility of chlorine dioxide in water. The aqueous ClO_2 solution will contain a small amount of chlorine (about 0.1 lb. Cl_2/lb. ClO_2). The remaining chlorine is recirculated to the combustion chamber.

The combustion of hydrogen and chlorine to form hydrogen chloride was discussed earlier in this report. The gases from the combustion chamber are divided into two parts. One is sent directly to the generator to provide the gaseous HCl. The other is sent to a scrubber where hydrochloric acid is formed and the excess hydrogen is purged from the system. The hydrochloric acid is used for the acidification of the chlorate liquor being fed to the generator.

Safety Problems

A question has arisen concerning the safety of the Chemech process as disclosed in the patent. This problem is concerned with the use of hydrogen as a diluent gas in the generator and absorber. Hydrogen and chlorine can form explosive mixtures and it is reasonable to expect that hydrogen could react violently with chlorine dioxide if initiated. Thus, the use of hydrogen as a diluent for chlorine and chlorine dioxide would seem to be a dangerous practice.

Some diluent gas in the generator is needed to keep the partial pressure of ClO_2 down to safe levels. Chlorine dioxide can decompose, and the rate of decomposition (and the associated violence) increases rapidly as the partial pressure of chlorine dioxide increases or as temperature is increased. A common rule of thumb in the industry is that handling of ClO_2 is relatively safe if the partial pressure is kept below 76 mm. Hg (10% by volume at atmospheric pressure). (Reference Solvay operations manual, 1955). Thus, some diluent gas is needed in the generator. The concern is with hydrogen gas being the diluent.

It is possible that the use of hydrogen as a diluent is an artifact of the patent. This usage was inferred from the process diagrams and descriptions in the patent and was not specifically claimed in the patent. Indeed, no mention of a diluent gas was made. Hence, the Chemech process may not actually operate with hydrogen as a diluent, especially since the problem can be avoided by relatively minor modifications of the process flow sheet. An example of such a system is shown in Fig. 9. This modification provides for scrubbing the small amount of chlorine from the hydrogen from the chlorate cells. The unneeded hydrogen is then removed from the system prior to the combustion chamber. Sufficient air could then be added at the combustion chamber to provide for dilution of the ClO_2. The inert gas would be purged from the system at the HCl scrubber. Thus, it is quite feasible for the Chemech process to operate without the use of hydrogen gas as a diluent.

In the Chemech process, chlorine dioxide is obtained as an aqueous solution since absorption in water is the method used to separate the ClO_2 from Cl_2. Gaseous chlorine dioxide could be obtained directly from the generator, but it would contain at least one-half mole of chlorine per mole of chlorine dioxide. If a chlorine-free ClO_2 gas stream is desired, chlorine dioxide would have to be stripped from the absorber solution. These restrictions are inherent in all Day-Kesting processes.

It remains to be determined if large amounts of chlorine gas (about 1/2 mole Cl_2 per mole ClO_2) can be tolerated in the oxidation step in holopulping. If large amounts of chlorine could be tolerated in gaseous-phase oxidation, then it is advantageous to modify the Chemech process to obtain gaseous ClO_2 directly. One possible modification is shown in Fig. 10. It may be noted that in this case it is not necessary to use hydrogen from the chlorate cells since adequate hydrogen would be available from the chlor-alkali cells alone. This is because the chlorine

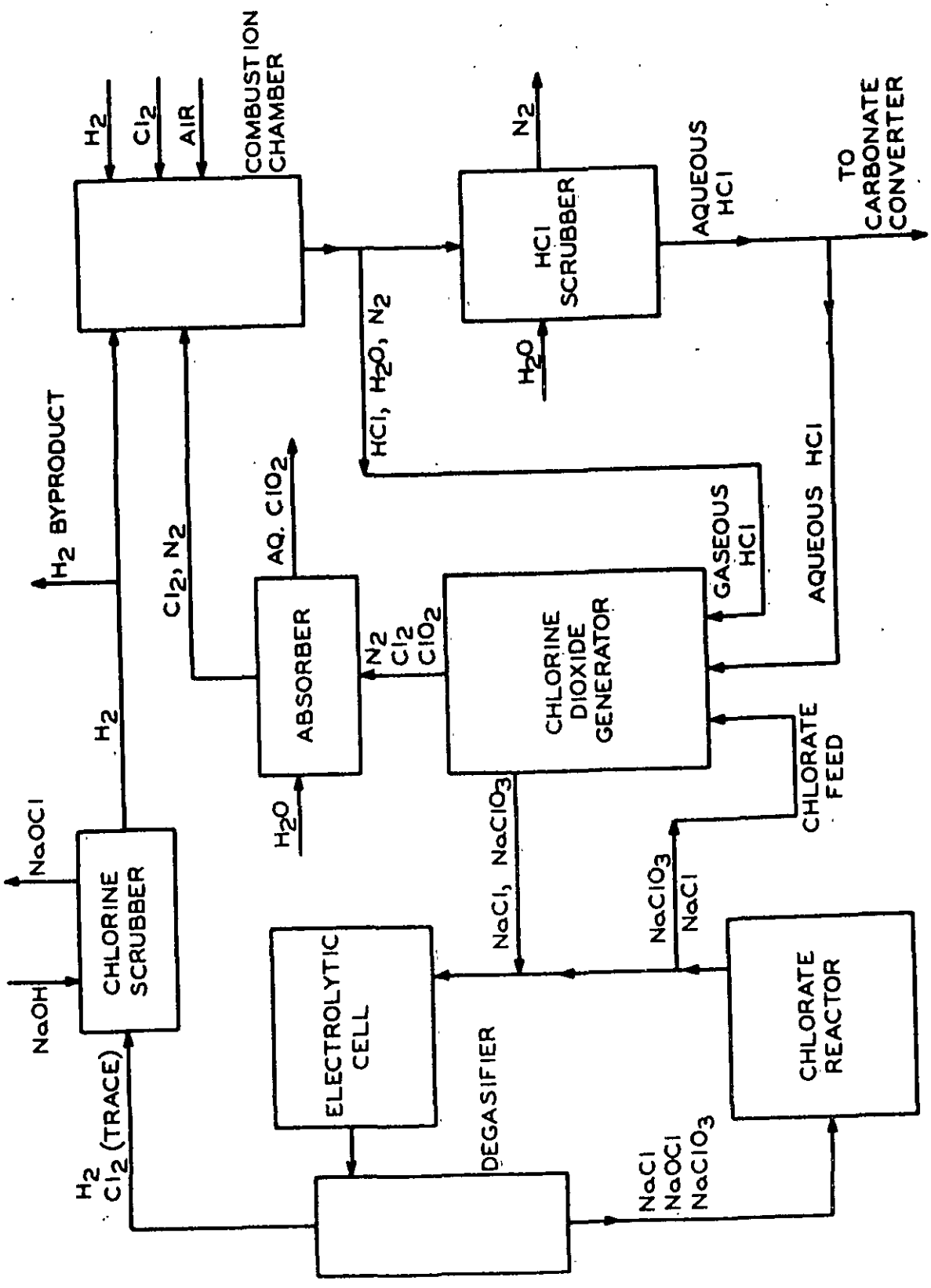


Figure 9. Modification of Chemech Process

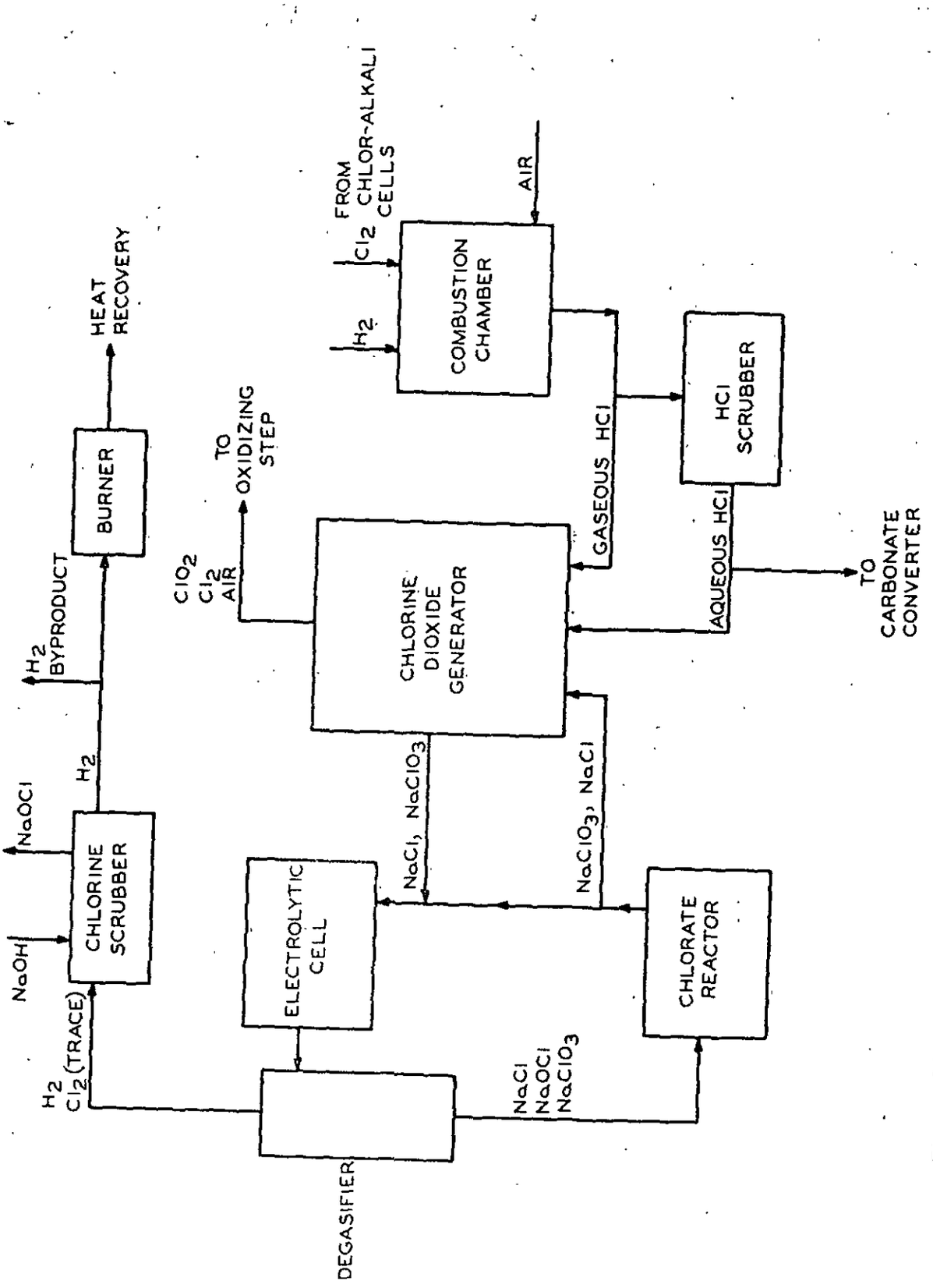


Figure 10. Modification of Chemech Process to Obtain Gaseous ClO_2 Directly

leaving the system (as Cl_2 and ClO_2) is equivalent to hydrogen chloride taking part in the reaction $NaClO_3 + 2HCl \rightarrow NaCl + {}^1/_2Cl_2 + ClO_2 + H_2O$. Since the reaction involves HCl, the chlor-alkali cells provide sufficient hydrogen.

The Chemech system is not the only means by which ClO_2 can be produced by the Day-Kesting process. For example, other types of chlorate cells could be employed. One restriction would be that these cells must provide for collection of hydrogen if relatively chlorine-free ClO_2 is desired since hydrogen from chlorate cells is needed to convert the chlorine formed by reaction of HCl with chlorate back to HCl. If the chlorine loop (as in Fig. 10) is open, and the mixture of ClO_2 and Cl_2 is directly usable, any chlorate cell could be used. An article by Casson, Crane, and Styan in the January 19, 1968, issue of Pulp and Paper Magazine of Canada listed five firms which offer sodium chlorate process and technology for on-site sodium chlorate production. They are Chemech, Casson and Crane, Vickers Krebs, Pacific Engineering, and Pechiney. Of these, all but the Casson and Crane cell provide for collection of hydrogen. Another variation would be to use methods other than Chemech's for carrying out the reaction of HCl with sodium chlorate. There is little information available in the literature on this possibility. Finally, it is conceivable that purchased sodium chlorate could be used for reacting with HCl to produce ClO_2. However, in this case it would be necessary to carry out the reaction to complete conversion of chlorate (as opposed to reacting only a portion of the chlorate and recirculating the remainder to the chlorate cells), and conditions would probably be reached where the undesirable side reaction,

$$NaClO_3 + 6HCl \rightarrow 3Cl_2 + NaCl + 3H_2O ,$$

would predominate. In summary, it appears that the Chemech system is the presently most promising approach to ClO_2 production for holopulping. This view is based

on the successful commercial operation of their chlorate cell and on their experience with the entire system at the pilot-plant level.

INTEGRATION OF PROCESS ELEMENTS

The preceding discussion has been concerned with some aspects of the components which would make up the holopulping process. In order to understand how all of these factors interact, and to make material and energy balances over the process, it is necessary to integrate all of these process elements into an overall process. At the present time, at least, there is no single holopulp process, but rather, many options are available. Many of these have been discussed above. There is, for example, the choice between an independent holopulping process and one tied to kraft production. In addition, there are possibilities of carrying out oxidations with either gaseous ClO_2 or aqueous ClO_2, using diaphragm cells or mercury cells, and using various ClO_2 generating methods. All of these possibilities must be considered so that the most promising approach to commercial holopulping can be assessed.

SELF-SUFFICIENT HOLOPULP PROCESS

The most desirable situation would be a process which is essentially independent of any other process. Such a process would have complete regeneration of the necessary cooking chemicals with no direct discharge of wastes to the environment. This can be approached through evaporation and combustion of the waste liquor, electrolytic chlor-alkali production, and ClO_2 generation by Day-Kesting processes incorporating electrolytic chlorate production. A typical flow diagram for such a situation is shown in Fig. 11. This particular diagram is based on:

a. aqueous-phase oxidation,
b. a single oxidation, extraction, hypochlorite sequence
c. low-temperature combustion
d. diaphragm cells for chlor-alkali production, and
e. modified Chemech process for chlorine dioxide production.

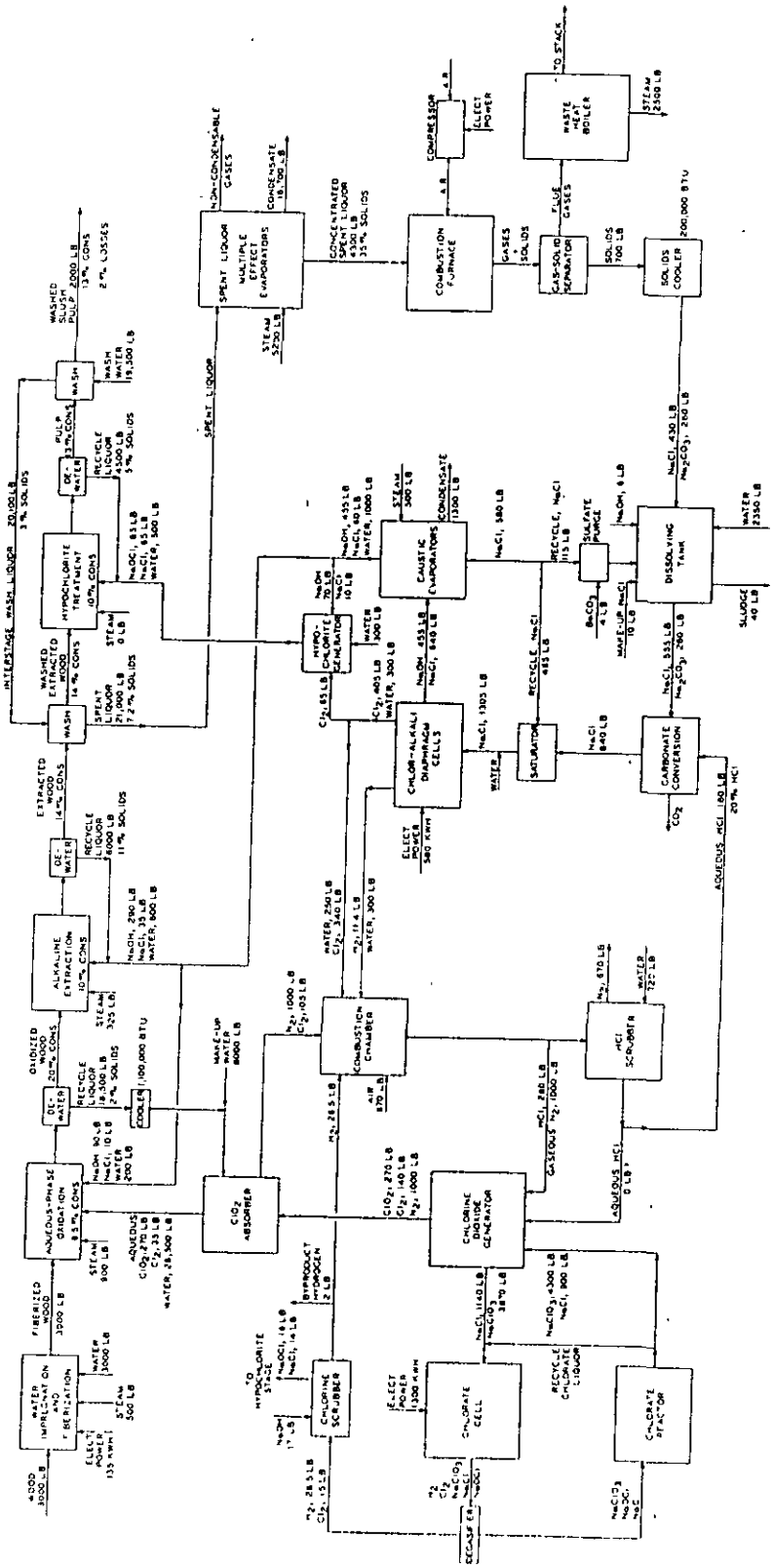


Figure 11. Typical Flow Diagram for Complete Holopulp Process

Material balance data are included on the flow diagram in Fig. 11. These data are quite interesting and provide a basis for discussing some of the important aspects of the process.

Water Balance

One of the obvious features is the low-concentration spent liquor which is obtained. This concentration is based on an assumed dilution factor of 3. Each of the pulping stages is provided with recycle of the liquor to minimize dilution, yet spent liquor concentration is still very low (7.2% solids). The critical factor affecting the spent liquor concentration is the ability to dewater the stock after each pulping stage. This determines the water load passing to succeeding stages and the amount of make-up water which must be added to the recycling liquor, hence the ultimate dilution of the liquor. In the example chosen, it was assumed that the stock was dewatered to a consistency of 20% after the oxidation step. (Consistency in these calculations considered only water and the o.d. "pulp". The effects of dissolved solids was ignored.) This assumption dominated the calculated value of the spent liquor concentration since it led to the introduction of 8000 lb. of make-up water into the system. In the remaining two pulping stages (extraction and hypochlorite) no make-up water is added. Only the steam used to raise the material to the desired reacting temperature and the water carrying the chemical enters the process. The drop in consistency between the oxidation stage and the extraction stage is due mainly to the removal of organic from the wood in the extraction step (and the way consistency is used here). It should be noted that the consistencies leaving these latter two stages are not really controllable parameters affecting the water balance except through the possibility of lowering them to the point where make-up water is added. Thus, even though it would be possible to dewater to a higher consis-

tency after the extraction step, for example, the extra liquor (above that shown) could not be recycled back since this would simply lead to an accumulation of liquor within the extraction step. This is not to say that the dewatering is limited to 14%, but any liquor removed above this consistency would have to be added to the spent liquor. While this might lead to some improvement in washing efficiency, it would not have any effect on the calculations of the water balance.

The critical parameter in this particular case is the consistency after dewatering in the oxidation step. The material after oxidation tends to have a character more like the original shredded wood as opposed to pulp. Thus, it is quite possible that it could be dewatered to a significantly higher extent, say 30% consistency. This has a profound effect on the whole water balance. Under the assumption that the consistency leaving the oxidation stage is 30%, the make-up water at this stage is reduced to about 3000 lb., a saving of 5000 lb. of water. This would allow the consistency after the extraction step to be raised to about 20%, and the consistency after the hypochlorite step to be about 19%. The wash water requirement would be reduced to 14,500 lb. of water, and the spent liquor would amount to 16,000 lb. at a concentration of 10% solids. This would save 600 lb. of steam at the evaporator at a steam economy of 3.2. It is thus obvious how critical the ability to dewater after the oxidation stage becomes. It is possible, under these conditions, that control of the water balance could shift to the ability to dewater after the extraction or hypochlorite step since this material is much more pulplike. The ease of dewatering to 20% consistency on a commercial scale would then become critical.

Chemical Balances

The flow of chemical around the system is, of course, determined by the dosing requirements. In this example, the ClO_2 requirement was taken to be 9%

on the original wood, with 3% NaOH used for buffering. The extraction step uses about 10% NaOH on the oxidized wood and the hypochlorite treatment about 2.5% on the wood. In addition, some chlorine enters with the ClO_2 and some NaCl with the caustic and hypochlorite solutions. The sodium and chlorine which are introduced appear in the spent liquor and are recovered as a mixture of sodium chloride and sodium carbonate. Sodium must be present in excess of chlorine on a mole basis in order to recover the chlorine in solid form. If the pulping conditions are such that this condition is not satisfied, then sodium hydroxide must be added to the spent liquor prior to combustion to provide the excess sodium. For the pulping conditions chosen for this example, the excess sodium requirement is satisfied.

About 700 lb. of NaCl and Na_2CO_3 are recovered per ton of pulp and are transmitted to the regeneration system. It is important to note that all of the sodium and chlorine are present as sodium chloride at one stage in the recovery system, namely the brine stream entering the chlor-alkali cells. The imbalance in the relative amounts of sodium and chlorine used in the pulping step is compensated for by the use of chlorine to form HCl to convert Na_2CO_3 to NaCl. Hence there are two distinct chemical loops - one involving the pulping reactions and the other HCl generation and carbonate conversion, which combine to provide an NaCl brine feed to the chlor-alkali cell. There is no essential difficulty in maintaining this balance. As the proportion of chlorine relative to sodium increases in the pulping zone, less carbonate is formed upon combustion of the liquor, and less chlorine (as HCl) is needed to convert the carbonate, and vice versa. If losses of sodium and chlorine are ignored and the furnace products are NaCl and Na_2CO_3, the system is completely self adjusting.

There are no inherent problems in supplying make-up chemical to compensate for sodium and chlorine losses. The exact make-up to be used would depend on the relative losses of sodium and chlorine. Sodium chloride would be used to

make up the amount of the element which is lost to the lesser extent, and either chlorine gas, Cl_2, or caustic soda, NaOH, would be used to supply the remainder. Thus, if the sodium loss exceeds the chlorine loss, NaCl make-up would supply the chlorine loss and part of the sodium loss. The remainder of the sodium loss would be from make-up NaOH. Similarly, if chlorine loss exceeds the sodium loss, NaCl would supply the necessary sodium make-up and part of the chlorine, and make-up Cl_2 would supply the remaining chlorine. Make-up sodium chloride would be added to the dissolving tank so as to be subject to the brine purification steps. Make-up chlorine could be added directly to the combustion chamber if desired, and make-up NaOH directly to the caustic stream from the caustic evaporator.

As was mentioned previously, a certain amount of NaCl enters with the caustic solutions. This amount of sodium chloride merely circulates around the pulping loop and does not take part in any reactions. It is primarily a function of the degree of evaporation of the caustic evaporation step since NaCl is dropped out as the caustic solution is concentrated. There does not appear to be any direct harm in this recirculating NaCl load (unless it adversely affects the pulping). The main effect would be a higher inorganic-to-organic ratio in the liquor which would influence the heating value of the liquor, and a greater opportunity for losses. This recirculating load passes through the chlor-alkali cell without being electrolyzed, and thus does not affect the power requirement. There is one restriction on the degree of caustic evaporation, and hence on the amount of dead-load salt circulating through the pulping loop. A certain amount of recycle salt (dropped out during caustic evaporation) is needed to provide for purging sulfate from the system and for controlling the degree of saturation of the brine entering the diaphragm cell. The caustic evaporation must be carried out <u>at least</u> to the extent that it provides that minimum.

As has been discussed previously in this report, this entire recovery system is predicated on obtaining NaCl and Na_2CO_3 as the inorganic products of the combustion of the spent liquor. However, in the context of the interactions of the various components of the system, there is an additional problem which should be mentioned. Because of the high yield of the pulping process, the amount of inorganic in the spent liquor to provide the energy for combustion is lessened. This may make it necessary to use auxiliary fuel to sustain combustion of the liquor. It would seem to be important to avoid the use of a fuel which contains sulfur. Any sulfur so introduced might well be recovered as Na_2SO_4 along with the NaCl and Na_2CO_3. Since sulfate ion must be controlled in the chlor-alkali system, any sulfur introduced as part of the fuel which would be converted to Na_2SO_4 would have to be removed by barium carbonate precipitation. This would become quite troublesome and expensive. Depending on the need for auxiliary fuel, and the availability and cost of a sulfur-free fuel, it may well be advisable to consider another alternative. This would involve carrying out a more drastic caustic extraction to remove more of the hemicelluloses from the pulp to provide a greater amount of organic having fuel value in the liquor.

The chlorine dioxide generation system which is shown in Fig. 11 is essentially the modification of the Chemech process discussed earlier. There are several possible interactions of this system with the chlor-alkali system which should be discussed. The first involves the use of a common combustion chamber for the generation of hydrogen chloride. HCl is a basic reactant in ClO_2 generation and is also required for converting Na_2CO_3 to NaCl in the chlor-alkali system. The potential problem arises through the introduction of air into the combustion chamber to provide nitrogen for dilution of the ClO_2 leaving the generator. Nitrogen is purged from the system at the HCl scrubber, and the amount of air required is that which is sufficient to provide this amount of

nitrogen. The amount of nitrogen purged is dependent on the ratio of HCl to nitrogen leaving the combustion chamber, and on the amount of aqueous HCl required. The ratio is dependent primarily on the degree of dilution desired for the ClO_2 leaving the generator. Because the diluent gas forms a closed circuit through the generator, absorber, and combustion chamber, it is important that combustion be complete in the combustion chamber. More specifically, all chlorine must react with hydrogen to form HCl, and the oxygen in the air must react with hydrogen to form water vapor. If all of the oxygen is not consumed, it will recirculate around the loop and compete with chlorine for the hydrogen. Thus, hydrogen must be supplied to the combustion chamber to a sufficient extent to react with all of the chlorine entering and with the oxygen in the air being supplied. There is no inherent problem (only one of control) if this hydrogen requirement is less than the total hydrogen generated in the chlorate and chlor-alkali cells. Such is the case in the example shown in Fig. 11. It should be noted that even this case is marginal since the excess hydrogen is only 2 lb. out of 40 lb. and no aqueous HCl was being fed to the generator. There appear to be three ways of overcoming this problem.

(1) The HCl for carbonate conversion could be generated in a separate combustion chamber. This would remove a large demand for aqueous HCl from the chlorine dioxide system and greatly reduce the amount of nitrogen purged, and hence the amount of air needed and the hydrogen combustion requirement.

(2) A hydrocarbon fuel could be burned in the combustion chamber to make up for a deficiency in hydrogen. This fuel would have to be essentially sulfur free. Care would need to be taken to ensure that the chlorine had reacted with hydrogen before introducing air and fuel into the combustion chamber.

(3) The nitrogen vented from the HCl scrubber could be returned to the combustion chamber or the gaseous loop. This would greatly minimize the need to introduce air into the combustion chamber.

The other interaction between the chlor-alkali system and the chlorine dioxide system lies in the possibility of using the wet cell gases from the chlor-alkali system as opposed to the use of dried, purified cell gases. Since the diaphragm cells operate at temperatures approaching the boiling point, a good deal of water vapor is carried along with the chlorine and hydrogen. If wet cell gases are used directly, this water is introduced into the ClO_2 system. The ability of the Chemech process to handle water inputs of this magnitude must be examined. Possible adaptations to remove water from the ClO_2 system would have to be weighed against methods for drying the gases from the diaphragm cell.

Operating Flexibility

One factor of great importance when considering the overall system is the degree to which various components can be divorced from one another to provide for the type of flexibility needed to operate the process on a commercial scale. To a large extent, this amounts to determining the parts of the system where storage is possible, and those parts where storage is not possible.

The pulping portion of the system consists of four distinct operations: fiberization, oxidation, extraction, and hypochlorite treatment. It is pertinent to ask whether these must be operated in single-train fashion or whether some decoupling between steps could be provided. The critical condition would appear to be the possibility of undesirable chemical reactions occurring which would degrade pulp properties. The shredded wood leaving the fiberizer would be hot and have a high moisture content. It could, in this state, be fed immediately to the oxidation reactor. If this shredded material is to be stored for any

appreciable time, it would probably have to be cooled. This could be accomplished by simply passing air through the material. This would have a tendency to dry the material which could cause problems in the oxidation step. In the process shown in Fig. 11, the "pulp" is dewatered after each step. This dewatered "pulp" could be temporarily stored between stages if undesirable chemical reactions do not occur. If storage were the main concern, the material could be washed to remove all active chemical and then dewatered. However, the resulting dilution of the spent liquor attendant on interstage washing would act against this procedure. Washing would be an integral part of the pulping procedure. Storage of interstage wash liquor would be no problem.

The evaporation and combustion steps can be dynamically decoupled from the remainder of the system by providing for storage of weak spent liquor, concentrated spent liquor, and solids from the furnace. The first two are a part of normal recovery practice. Storage of the inorganic from the combustion step is predicated on carrying out the combustion at temperatures below the melting point of the salts. If this is not the case, a smelt dissolving tank would be required and the combustion operation would be strongly coupled to the chlor-alkali system.

In the chlor-alkali system itself, several storage locations are available to provide the necessary flexibility. Aqueous HCl storage would provide a reservoir of hydrochloric acid for carbonate conversion. Strong brine storage, immediately preceding the cells, would decouple the cells from the brine purification system. Storage could be provided for the caustic solution leaving the caustic evaporators, as well as for the hypochlorite solution. Chlorine storage could constitute a problem. If a significant chlorine storage capacity is required, it would probably be necessary to dry and purify the wet cell gas and store the chlorine as either compressed gas or liquid chlorine. Since the chlorine produced at the diaphragm cells is used for chlorine dioxide production and (as

HCl) for carbonate conversion, the need for chlorine storage depends strongly on the chlorine dioxide system.

Operating details of the Chemech process are not currently known to us and there is thus some uncertainty concerning the operating flexibility of this system. Since aqueous ClO_2 is used (in Fig. 11) a limited amount of chlorine dioxide could be provided through storage of the aqueous solution leaving the absorber. However, the low concentration of this solution, the tendency for ClO_2 to decompose, and the presence of organic material in this solution from the recycled liquor would all act to make this an unfavorable means of providing flexibility. It would appear that the chlorine dioxide system must operate on a demand basis, that is, it must supply ClO_2 continuously at the rate at which it is needed. This would place the strongest demands on the response characteristics of the chlorine dioxide generator itself. The major reactants are sodium chlorate and hydrogen chloride. Chlorate can be stored effectively (in the Chemech process) in the recirculating chlorate solution by building up the chlorate concentration at the expense of sodium chloride. Thus, a reservoir of chlorate is available to meet changes in demand. Similarly, HCl can be stored as an aqueous solution of hydrochloric acid. The big unknown at present is the role played by gaseous hydrogen chloride as opposed to hydrochloric acid in the generator. If hydrochloric acid can be used to meet load demands and the response of the generator itself is rapid, then the process would have the necessary flexibility. However, if gaseous hydrogen chloride plays a critical role, then it would be necessary to either store gaseous hydrogen chloride under pressure as a reserve, or to store chlorine and hydrogen and adapt to load variations by changing chlorine (and hydrogen) feed rates to the combustion chamber.

In general, the process does appear to provide for a good deal of flexibility in operating. The chemical recovery system is essentially self adjusting with regard to pulping chemical requirements over a wide range. The most critical interaction would appear to be between the ClO_2 supply system and the oxidation step. In the worst case, this latter problem would require storage of chlorine and hydrogen and a rapidly responding generator. Although this might complicate the process, there do not seem to be any inherent difficulties.

Process Requirements

The major process inputs required for this process are wood, water, make-up chemical, steam, and electrical power. In addition, there is a possible requirement for auxiliary fuel at the combustion furnace plus the barium carbonate needed for purging sulfate, and sodium dichromate added to the chlorate cells.

There are three directly definable requirements for electrical power; at the chlorate cells, at the chlor-alkali cells, and for fiberizing the wood. In addition, if fluidized bed combustion of the spent liquor is used, either electrical power or a steam-driven turbine would be required for supplying compressed air to the furnace.

The largest power demand is at the chlorate cells since six faradays re required for each mole of chlorate produced. Approximately 1300 kw.-hr. are equired per ton of pulp. The power needed by the chlorate cells should be irectly proportional to the ClO_2 requirement since the chlorate production is rectly related to chlorine dioxide production. Three efficiencies affect the wer requirement at the chlorate cells. The first efficiency governs the ectrolytic production of chlorate in the chlorate cells and chlorate reactor. e second efficiency involves the conversion of chlorate to ClO_2 (as opposed to

conversion to chlorine by the undesired side reaction) in the generator. The third efficiency involves the absorption of ClO_2 in the absorber since any unabsorbed ClO_2 will be destroyed in the combustion chamber. The value of 1300 kw.-hr. is for an overall efficiency (combining the three listed above) of 50%, based on the theoretical requirement of 2.4 kw.-hr. per lb. ClO_2 given in Progress Report Seven.

The second largest power requirement is at the chlor-alkali cells. This value will be directly proportional to the requirement for caustic soda (as such, and for preparing hypochlorite) in the pulping steps, and will be independent of the amount of ClO_2 used (as long as sodium is used in excess of chlorine on a mole basis). The figure used for power consumption, 580 kw.-hr. per ton of pulp, is equivalent to 2850 kw.-hr. per ton of chlorine. This is reasonably close of published values for diaphragm cells and may be slightly on the high side.

A third power requirement is for fiberizing the chips prior to the chemical pulping steps. The value of 135 kw.-hr. used in Fig. 11 is based on a power requirement of 5 horsepower-days per ton of fiberized wood. This value is an estimate and could be off significantly. However, this power requirement is small compared to others in the system.

For the three defined electrical requirements, the electrical power is about 2000 kw.-hr. per ton of pulp. Allowing for other power demands in the process, and making allowances for higher efficiency in the chlorine dioxide system, it would appear that a complete holopulp system could require from 2000 to 2500 kw.-hr. per ton of pulp. This is a heavy electrical requirement, due mainly to the use of electrolytic chemical recovery schemes. For this reason, availability of low-cost electrical power would be a major factor in locating a holopulp mill.

The process requires a good deal of steam for evaporation of spent liquor and the caustic cell liquor as well as in the pulping steps. Some steam may also be required in the ClO_2 generator. The largest steam requirement is for spent liquor evaporation. In Fig. 11 5200 lb. of steam are required at a steam economy of 3.2. The actual amount of steam required for this operation will depend on the number of effects used (and the resultant steam economy) and the concentration of the spent liquor. Another large steam requirement is for caustic evaporation. In the example chosen, 500 lb. of steam would be needed at a steam economy of 2.6. This value is dependent on the degree of evaporation of the caustic and on the amount of water evaporated in the cell itself. Some steam could be needed to bring the brine up to the desired cell inlet temperature. A significant consumption of steam occurs in the oxidation step. This steam is used to bring the reaction mass up to the desired oxidation temperature. The value is high because it is assumed that the liquor to the ClO_2 absorber is chilled to 50°F. in order to improve the solubility of ClO_2. There is an attendant cooling requirement on the recycled liquor at this step. Steam is also required for the fiberization step. The value of 500 lb. in Fig. 11 includes that which would be used in purging air from the wood as well as that used to bring the chips up to fiberizing temperature. Finally, there is the steam used in bringing the material up to reaction temperature in the extraction step. Steam may not be needed for the hypochlorite treatment since the hypochlorite reaction is carried out at a lower temperature than the extraction step.

The total of all steam inputs listed is about 7500 lb. of steam per ton of pulp. This would appear to be a high estimate since the steam requirement for spent liquor evaporation could certainly be lowered. The estimate for steam for fiberizing is probably high also. However, it is likely that in any event the steam requirement would probably be on the order of 5000 lb. per ton of pulp.

This is a high steam requirement, particularly in view of the relatively low energy value of the spent liquor. Base on assumed heating values for the organic fraction of the spent liquor, it is estimated that the amount of steam generated with a waste heat boiler on the combustion furnace flue gases would be about 2500 lb. of steam per lb. of pulp. Thus, about 2500 lb. of steam would be needed from an auxiliary fuel boiler. Combustion of the by-product hydrogen would not affect the steam requirement to a great extent. This is also true of the heat given off in the HCl combustion chamber. These latter two are possible sources for energy recovery, however.

Make-up chemical requirements have already been discussed to some extent. The major make-up chemical would be sodium chloride, ordinary salt. Either chlorine gas or caustic soda would then be used to make up for differences in relative loss rates of chlorine or sodium. Amounts would tend to be small. If the losses are about 10% of the circulating load, about 70 lb. of NaCl make-up would be needed per ton of pulp. Chlorine or caustic soda make-up would run much less, probably about 10 lb. per ton of pulp.

Process water is another major requirement. Water enters the process at several points. The major water addition is wash water - 19,500 lb. in the example in Fig. 11. Next comes 8000 lb. of water added to the oxidation step loop. There is also water added during impregnation in the fiberizing step, to the recovered solids dissolving tank, at the HCl scrubber, and at the hypochlorite generator. Adding up the water estimates as shown in Fig. 11 gives a total of 34,000 lb. water or 4000 gal. per ton of pulp. This value is of course highly dependent on consistency control and washing practices in the pulping steps.

The last major raw material is the wood. Under the conditions chosen for the pulping step, it is expected that the yield would be about 67%. Thus,

3000 lb. of chips would be required per ton of pulp. These figures are based on laboratory work on aspen and red maple, and should be applied with care to other species.

Process Effluents

With increasing concern about pollution, it is necessary to devote attention to the effluent from this process. One of the major hopes for this process is that by providing a sulfur-free system pollution problems would be minimized. It is pertinent to examine the validity of this contention. In this connection, it is convenient to divide effluents up into gaseous, aqueous, and solid effluents.

The major gaseous effluent would be the flue gas from the liquor combustion furnace. Ideally, if the combustion proceeded perfectly, the flue gas would consist only of CO_2, N_2, O_2, and water vapor. However, the possibility that chlorine compounds, particularly HCl gas, might be present is significant. This possibility must be thoroughly examined since it is not considered realistic to replace a sulfur emission problem with a chlorine emission problem. Particulate emission, particularly sodium chloride fume is also a possibility. It is felt that the composition of the flue gas produced by burning holopulp spent liquor is the greatest single unknown which must be resolved concerning this process.

Other sources of gaseous emissions include noncondensible gases from the spent liquor evaporators, CO_2 liberated during carbonate conversion, possibly by-product hydrogen, and gases liberated at the discharge from the oxidation step. The most serious potential problem would appear to be with the noncondensible gases from the spent liquor evaporators. This could include odorous or toxic

chlorine-containing compounds. This possibility must be examined in detail. Possible gas emissions at the oxidation discharge could be a problem, particularly if unreacted ClO_2 or Cl_2 is present. It may be necessary to carry out the oxidation step discharge in a completely closed system. Liberation of CO_2 during carbonate conversion should not constitute any problem since venting could be easily done. If the excess hydrogen is not recovered and sold as a by-product and if it is not burned in some furnace for energy recovery, it must be safely disposed of. This could be done either by flaming it off or by diluting it with air below hazardous concentrations and discharging it to the atmosphere.

The major aqueous emission is an indirect one, namely the material leaving the process with the pulp. All of the organic, sodium, and chloride which is not washed out leaves the process with the slush pulp. This would eventually add to effluent burdens on subsequent operations. Thus, incomplete washing, in effect, constitutes an effluent problem. The other major aqueous effluents are the condensates from the spent liquor evaporators and the caustic evaporators. The major problem would probably be with the spent liquor evaporator condensate since it could be contaminated with organic or chlor-organic compounds. The extent of this problem must be investigated.

The major solid effluent would be the sludge from the recovered solids dissolving tank. This material would include barium sulfate, calcium carbonate, magnesium hydroxide, unburned carbon, silica, and other foreign materials. It is estimated to amount to about 40 lb. per ton of pulp.

Overall Considerations

The process which is illustrated in Fig. 11 is essentially quite straightforward and uncomplicated. The simplicity of the process is possibly better shown

by the schematic diagram in Fig. 12. In this figure, detail is suppressed to show the essence of the marriage between pulping and recovery. It is clearly seen that the whole process converges to a pure NaCl stream entering the chlor-alkali cells. Thus, entering and leaving the chlor-alkali cells, sodium and chlorine are on a one-to-one correspondence on a mole basis. However, the entire sodium loop is through the pulping step, whereas only a part of the chlorine goes through the pulping step. The difference is reacted to HCl and used to convert carbonate to chloride and maintain the balance.

The major requirement for recovery is that sodium be used in excess of chlorine in the pulping step so as to ensure sufficient sodium to recover all of the chlorine as NaCl during burning. This excess of sodium shows up as Na_2CO_3 leaving the furnace. Other than this requirement, the recovery system makes no demands on chemical usage. These are determined by economics and by the pulping effectiveness. Hence, amounts of the four reagents - ClO_2, Cl_2, NaOCl, and NaOH - can be varied to a wide degree, subject only to the limitation that sufficient NaOH be used to provide an excess of sodium.

The most expensive chemical used in the process is chlorine dioxide, due to the large power needed (for chlorate production) and to the expensive system required for generation. Thus, it is worth while to examine the possibilities of replacing some ClO_2 with Cl_2 or hypochlorite. There is a direct benefit if any or almost all of the chlorine used for carbonate conversion can be used in the oxidation step. If the caustic usage remained constant, this chlorine would be obtained without any increase in power requirement, and the saving in ClO_2 which might be replaced by this Cl_2 would be a direct gain. The situation is less direct if the amount of hypochlorite is increased since caustic is used to form the NaOCl. If the amount of caustic used in the extraction is reduced

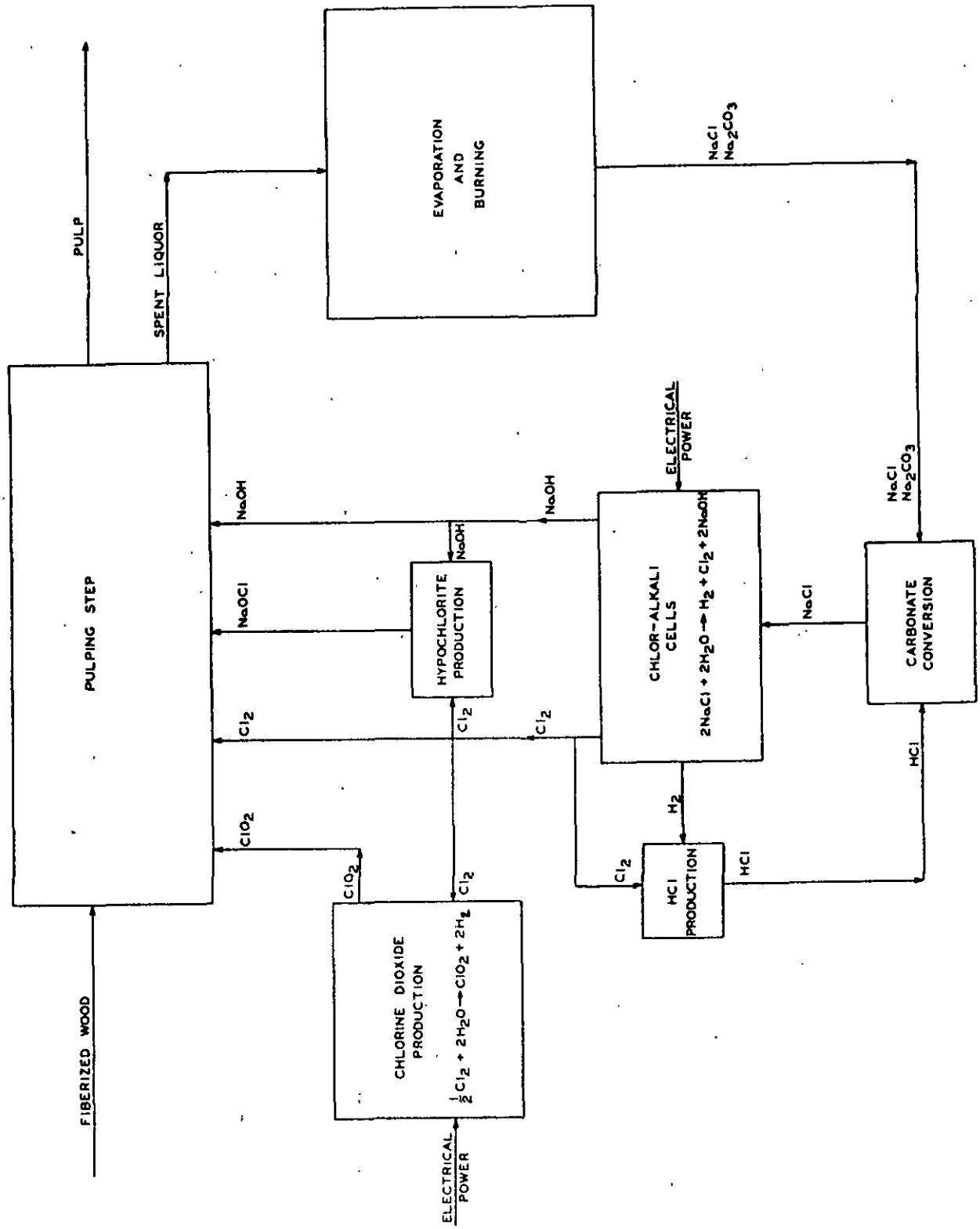


Figure 12. Simplified Schematic Diagram of Process

proportionally to maintain total sodium constant, any reduction in ClO_2 due to increased hypochlorite use would be a direct benefit. However, if the amount used for caustic remains constant, increasing the amount of hypochlorite would increase the power required at the chlor-alkali cell. In this case, a power balance would be needed between the electrical energy saved in the ClO_2 system and the extra electrical energy used in the chlor-alkali cells.

In general, any rerouting of the chlorine used for carbonate conversion into the pulping step is advantageous provided that this is compatible with desired pulp properties and good recovery during combustion of the liquor. Changes that involve an increase in caustic production require a comparative economic evaluation between the ClO_2 system and the chlor-alkali system.

One final comment should be made with respect to this system. It is independent of the sequence of steps in the pulping operation. Thus, if pulping were carried out using H-E-D rather than D-E-H, there would be no effect. In fact, any combination of stages involving chlorine, chlorine dioxide, caustic, and hypochlorite is compatible with the rest of the system provided that sodium is present in excess of chlorine. The only restriction is complexity and spent liquor dilution (this is, of course, a very significant restriction).

PERMUTATIONS ON SELF-SUFFICIENT PROCESS

The holopulp system shown in Fig. 11 is, of course, by no means the only possible self-contained holopulping process. Many permutations of arrangement are possible which still maintain the essence of the process. Some of these variations have been discussed earlier when the different elements of the process were considered. The pulping step itself is not limited to the sequence oxidation-extraction-hypochlorite with oxidation carried out with chlorine dioxide. Chlorination could be used in conjunction with oxidation or even in a separate stage,

as, for example, in C-E-D-E-H. Alternatively, the basic oxidation sequence could be multistaged as in D-E-D-E-H. A wide variety of sequences are compatible with the basic nature of the process. Various methods of carrying out the evaporation and combustion step are available, ranging from the minimum evaporation-low temperature combustion approach shown in Fig. 11 to evaporating to high solids concentrations using forced circulation or direct contact evaporation and high temperature combustion producing a smelt. In the chlor-alkali system, mercury cells could be used in place of diaphragm cells. This would involve changes in the brine purification and saturation system, but would not greatly affect the other elements of the process. Another permutation would involve the use of other Day-Kesting type processes for ClO_2 production instead of the Chemech process.

Gaseous Oxidation

One permutation which deserves serious consideration is the use of gaseous ClO_2 or Cl_2-ClO_2 mixtures in the oxidation step. This variation has a profound effect on many of the other operations of the process which should be considered in detail. In evaluating the effectiveness of gaseous oxidation, it is pertinent to begin with the generation of chlorine dioxide. Chlorine dioxide is produced as a gas in the chlorine dioxide generator. By the nature of the reaction employed by all Day-Kesting type processes,

$$2HCl + NaClO_3 \rightarrow ClO_2 + \frac{1}{2} Cl_2 + NaCl + H_2O$$

the gas leaving the generator will be contaminated with chlorine gas. At a minimum, the generator gas will contain 1/2 mole of chlorine gas per mole of chlorine dioxide, or 0.526 lb. of chlorine gas per lb. of chlorine dioxide. The ClO_2 and Cl_2 are carried from the generator by the inert diluent gas. Normally the ClO_2 is separated from the chlorine by absorbing it in water. Chlorine

dioxide has a solubility in water about one order of magnitude greater than chlorine, and the bulk of the chlorine passes through the absorber. In the Chemech process, this unabsorbed chlorine gas is recycled to the combustion chamber to be reused.

The major question to be faced when considering gaseous-phase oxidation is whether or not it is necessary to separate the chlorine dioxide from the chlorine in the generator gas. If the oxidation step requires chlorine dioxide relatively free of chlorine, it would be necessary to go through the separation step. On the other hand, if the oxidation step can utilize a gas containing about one-half pound of chlorine gas per pound of ClO_2, then the generator gas could be used directly in the oxidation step. This is a very important factor. The major advantage of using gaseous oxidation would be obtainable only if the generator gas could be used directly. The reason is the added complexity (and costs) of the separation step. Consider what is required to carry out a gaseous oxidation with a relatively pure ClO_2 generated by a Day-Kesting reaction. The generator gas would be passed through an absorber where the ClO_2 would be solubilized and the Cl_2 would pass through. Separation would be achieved at the cost of putting the ClO_2 into aqueous solution. In order to carry out a gaseous oxidation it would be necessary to strip the ClO_2 from the absorber solution in another stripping tower. It is likely that the absorbant solution would be heated at the stripper to facilitate the stripping of ClO_2 and would then have to be cooled before being returned to the absorber. The addition of a stripping tower plus the need to heat and cool the recirculating liquor would tend to nullify any advantages of using gaseous oxidation in the pulping step.

On the other hand, if large amounts of chlorine can be tolerated so that the generator gases can be used directly in the oxidation step, both the

pulping step and the chlorine dioxide generation step are simplified. The water balance is favorably affected in the pulping portion of the system, and the gas loop is opened in the chlorine dioxide system. In addition, there is the possibility that the use of a good deal of chlorine would reduce the amount of chlorine dioxide required for oxidation. The use of generator gases directly for oxidation has a profound effect on the balances over the whole loop. A flow diagram with material balance data is presented in Fig. 13 for the case of direct gaseous oxidation. In this example, the chlorine used is assumed to reduce the ClO_2 requirement by the oxidation equivalent of the chlorine. This reduces the ClO_2 demand from 9% on the wood to 7.5%.

It is of interest to compare the values shown in Fig. 13 with those in Fig. 11. Caution must be used in interpreting these results since all changes are not directly associated with a change from aqueous-phase oxidation to direct gaseous-phase oxidation. It may be noted that the electrical energy requirement at the chlorate cells is reduced from 1300 to 1080 kw.-hr. This is a direct consequence of the assumption that the chlorine replaces the oxidation equivalent of ClO_2. The power required for the chlorate cells is directly proportional to the amount of chlorine dioxide required. The power requirement at the chlor-alkali cells remains the same, 580 kw.-hr., since the caustic requirement was unchanged. In the example shown in Fig. 13, that caustic formerly used as a buffer in the aqueous oxidation case was added to the extraction, thus increasing the amount of caustic used in the extraction step from 290 to 380 lb. Under the conditions shown in Fig. 13, the sodium-chlorine ratio in the spent liquor is still favorable for recovery, although the excess of sodium has been reduced. This is apparent in the reduction in the amount of Na_2CO_3 reaching the dissolver from 260 to 160 lb., and the concordant reduction in the HCl required for carbonate conversion from 180 to 110 lb. The remainder of the chlor-alkali system is

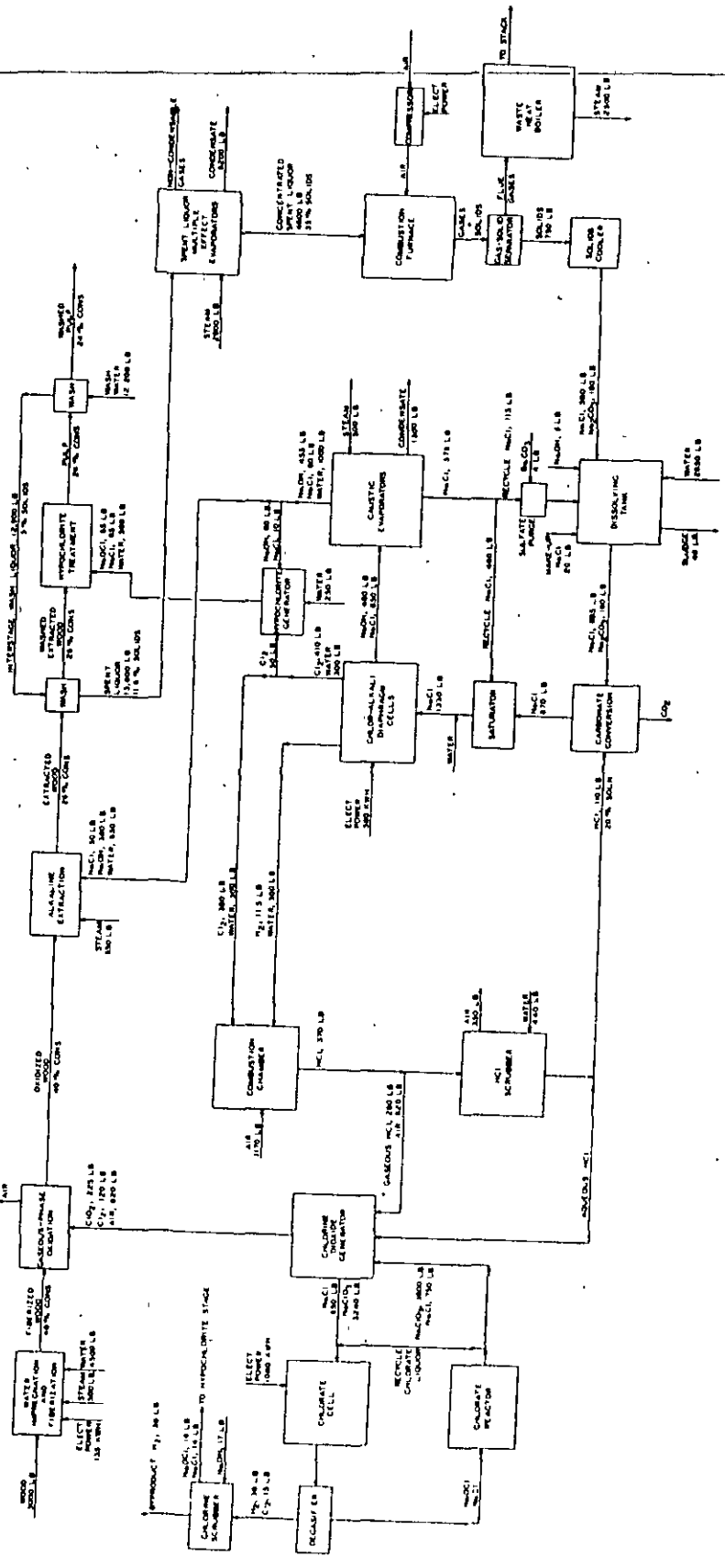


Figure 13. Typical Flow Diagram Using Gaseous Oxidation

unaffected by the change in the pulping step. The slight differences in values between Fig. 11 and Fig. 13 are the result of accumulated round-off errors in running the material balance and are not significant.

The water balance is much more favorable in the case shown in Fig. 13 than in Fig. 11. Solids concentration in the spent liquor is 11.6% as compared with 7.2% and the amount of steam required to evaporate to 35% solids at a steam economy of 3.2 is reduced 2300 lb. from 5200 to 2900 lb. This benefit cannot be ascribed entirely to the change from aqueous-phase to gaseous-phase oxidation, even though this change makes the increase more likely. When gaseous-phase oxidation is used, the water balance burden is simply shifted downstream in the process to the extraction, hypochlorite, and washing steps. In the example shown in Fig. 13, it was assumed that the only dilution was from water used to carry the chemicals plus a dilution factor of 3 during washing. Several factors are necessary in attaining this goal. Consider first the extraction step. The oxidized wood enters at 40% consistency and is taken to leave at 26% consistency with the only water addition being 850 lb. from the caustic solution and 350 lb. of steam. This is obtainable if it is possible to properly mix the caustic solution with the oxidized wood in a sufficiently uniform manner at the high consistency conditions at the extractor entrance. If this is impossible, the extractor could be operated at lower consistencies where good mixing is obtainable by dewatering the material leaving the extractor and recycling the liquor. In this latter case, it would be necessary to dewater to 26% consistency in order to avoid dilution water at the extraction step. Similar comments apply to the hypochlorite step and also to washing. Either special high-density washing techniques would be required or a drum washer system combines with a dewatering press with recycle of the expressed water into the wash system. The essence of this discussion is that the water balance chain is only as strong as its weakest

link. Converting the oxidation stage from aqueous ClO_2 to gaseous ClO_2 does not automatically solve the spent liquor concentration problem. It does provide the opportunity of attaining more concentrated spent liquors. It is worth pointing out that the final spent liquor concentration shown in Fig. 13 is probably close to the maximum obtainable with this process at the 65% yield range. Conditions applied to the extraction, hypochlorite, and washing steps to attain a concentration of this level are already quite severe. It may be noted that one benefit in converting from aqueous to gaseous oxidation is the elimination of the heating steam for the oxidation step (about 900 lb.).

The third factor noticeable in comparing Fig. 13 to Fig. 11 is the pronounced simplification of the chlorine dioxide generating system. Not only is the ClO_2 absorber eliminated, but also the gas loop is opened. Diluent gas is introduced into the combustion chamber, flows through the generator, and is exhausted at the oxidation reactor. Thus, coupling problems associated with the closed gas circuit are eliminated. Since none of the hydrogen produced at the chlorate cell is needed for reaction with chlorine, it can be treated to remove trace amounts of chlorine and then sold as by-product, sent to the liquor combustion furnace to aid in maintaining combustion, or burned elsewhere for its heating value.

It is evident that there are several distinct advantages in direct use of ClO_2 generator gases in the oxidation step.

1. The ClO_2 absorber, along with the need for chilling the absorbing liquor and reheating in the oxidation step, is eliminated.

2. Open-circuit operation of the gas side of the ClO_2 generating system provides for straightforward use of air as a diluent gas.

3. All of the hydrogen produced at the chlorate cells is available for use as a by-product or as a fuel, since it is not needed for burning with air or chlorine in the combustion chamber.

4. It provides an opportunity to carry out the pulping steps in such a manner as to obtain maximum spent liquor concentrations with the attendant reduction in evaporator size and steam requirements.

5. It provides for possible reduction in ClO_2 requirement if its oxidation equivalent can be used.

There are also some potential disadvantages to this approach.

1. The use of large amounts of chlorine in the oxidation step may lead to undesirable degradation of pulp properties.

2. There may be difficulties in design and operation of an oxidation reactor employing moist shredded wood and two reactive gases.

3. There is a potential air emissions problem at the vent of the gaseous oxidation reactor if unreacted chlorine or ClO_2 are present.

4. By reducing the excess of sodium in the spent liquor, emission of chloro compounds during evaporation and combustion of the spent liquor may be accentuated.

The potential advantages of the direct gas-phase approach to oxidation are sufficient to warrant further study of this possibility.

Holopulping with Incomplete Recovery

The preceding discussion has been concerned with complete holopulping processes, that is, systems with full chemical recovery and no by-product or major

effluent streams. These systems are based on electrolytic production of chlorine and caustic soda and on Day-Kesting processes for chlorine dioxide production which incorporate electrolytic chlorate production. These complete systems would obviously require large capital expenditures for chlor-alkali production and ClO_2 generation. It is conceivable that holopulping might be carried out without complete chemical recovery and regeneration. This could be especially true if a relatively small production was required. Such operation could be done in conjunction with a kraft mill or even separately, provided that suitable means for disposing of effluents were available. This is also a factor in considering holopulping on a pilot-plant scale since certain key aspects of the process could be piloted without constructing the entire system.

The possibilities for holopulping with incomplete recovery will now be examined. Because of pollution restrictions, the minimum requirements for any holopulping process would be the pulping steps themselves and means for disposing of the spent liquor. Because the liquor would contain a significant amount of chlorine compounds, direct addition of holopulp spent liquors to kraft spent liquors does not appear feasible. Hence, the minimum process requirements are the pulping steps including washing, evaporation, and burning of the spent liquor. The solids recovered from combustion would be disposed of in some manner. This would still leave the question of cooking chemicals. It is assumed that the necessary caustic would have to be purchased. Hypochlorite could be purchased or could be generated on site from purchased or by-product chlorine. Chlorine dioxide, on the other hand, would have to be generated on site. It is assumed that this would be done with conventional processes using purchased sodium chlorate in order to minimize capital costs.

There remains a good deal of variation in the limited process described above. This variation arises mainly from the choice of ClO_2-generating processes, aqueous or gaseous holopulping, and the use of chlorine in the oxidation step. These factors are interrelated since the choice of conditions for the oxidation system will strongly influence the selection of a ClO_2 generation process. There are four chlorine dioxide processes to consider - Solvay, Mathieson, R-2, and Erco R-3 or Hooker SVP (these latter two are essentially the same), and three oxidizing conditions -- aqueous-phase ClO_2, and gaseous-phase ClO_2, and gaseous-phae ClO_2-Cl_2.

Both the Solvay and Mathieson processes produce a nearly pure ClO_2 and would be suitable for either gaseous - or aqueous-phase ClO_2 oxidations. Each has a generator effluent consisting of a concentrated sulfuric acid solution containing sodium sulfate and residual chlorate to be utilized or disposed of. The R-2 process produces a ClO_2-Cl_2 mixture which would be suitable for gaseous ClO_2-Cl_2 oxidations. By absorbing the ClO_2 in water a solution is produced which is suitable for aqueous ClO_2 oxidations provided that a use for the unabsorbed Cl_2 is found. Under typical holopulping conditions, the by-product chlorine would far exceed that needed to produce hypochlorite. This process also has an effluent consisting of a solution of sodium sulfate in concentrated sulfuric acid. The R-3 process produces a ClO_2-Cl_2 mixture diluted with water vapor under vacuum. The ClO_2 is absorbed in water separating it from the Cl_2. Because of the low pressure conditions in the generator, it does not appear to be feasible to use this process for direct gaseous ClO_2-Cl_2 oxidations. Its use for aqueous ClO_2 oxidations is complicated by the same problem of utilizing the chlorine as the R-2 process. The R-3 process does have the advantage of having an effluent of sodium sulfate only without sulfuric acid.

A correlation of the various generation processes with oxidation conditions showing the advantages and disadvantages of each is given in Table XIII. In interpeting this table, it must be remembered that water balance restrictions still hold, and aqueous oxidations will involve a recycling liquor being chilled and reheated to reaction temperature.

It is evident that there are no really good combinations. The R-3 or SVP processes would be suitable only for aqueous-phase oxidations. However, there is the problem of what to do with the chlorine that is generated. The complexity of these processes coupled with the complexity of aqueous-phase oxidation would appear to outweigh the advantage of a generator effluent consisting of solid Na_2SO_4. The R-2 process would be suitable for gaseous-phase oxidations using the ClO_2-Cl_2 mixture as generated. Like R-3, it suffers from a chlorine disposal problem with aqueous oxidations. The amount of H_2SO_4 in the effluent is highest with this process. This would not be an advantage in holopulping. There appears to be relatively little to choose between in the other processes. Each has about the same effluent problems and generates a nearly pure ClO_2 for use in either aqueous or gaseous phase. Considering all of the possibilities, the most promising approaches would appear to be either gaseous- or aqueous-phase oxidations using either the methanol (Solvay) or SO_2 (Mathieson) process or a gaseous ClO_2-Cl_2 oxidation using the R-2 process.

The most favorable case would probably be a gaseous ClO_2 oxidation using either the Solvay or Mathieson process. Figure 14 shows a flow diagram with material balance data for holopulping with incomplete recovery based on gaseous oxidation and the Mathieson ClO_2 process.

TABLE XIII

COMPARISON OF ClO_2 GENERATION PROCESS

Process	Gases Produced	Reactants, lb./lb. ClO_2		Effluents, lb./lb. ClO_2		Comments	Conditions Most Suited for
Solvay	ClO_2	$NaClO_3$	1.80			Simple, low-cost process. Acid effluent.	Aqueous ClO_2
		H_2SO_4	2.90	H_2SO_4	1.70		Gaseous ClO_2
		NaCl	0.10	Na_2SO_4	1.30		
		Methanol	0.21	Formic acid.			
Mathieson	ClO_2	$NaClO_3$	1.75			Chlorine could adsorb in water or be used for hypochlorite formation.	Aqueous ClO_2
		NaCl	0.18	Na_2SO_4	1.40		
		H_2SO_4	1.75	H_2SO_4	1.70	Relatively simple process.	Gaseous ClO_2
		SO_2	0.60	Cl_2	0.10	Acid effluent.	
R-2	ClO_2 + 1/2 Cl_2	$NaClO_3$	1.66	Na_2SO_4	2.30	Simple process, relatively low capital cost.	Gaseous ClO_2-Cl_2
		NaCl	0.95	H_2SO_4	3.20	Heavy H_2SO_4 requirement and also in effluent.	
		H_2SO_4	4.80	Cl_2	0.57	Absorption in water yields chlorine disposal problem.	
Hooker SVP or Erco R-3	ClO_2 + 1/2 Cl_2	$NaClO_3$	1.66			More complicated, higher capital cost system.	None
		NaCl	1.14	Na_2SO_4	2.50	No sulfuric acid effluent.	(At best, aqueous ClO_2.)
		H_2SO_4	1.73	Cl_2	0.73	Absorption of gases in water gives chlorine disposal problem.	
						Low pressure in generator, gases diluted with steam.	

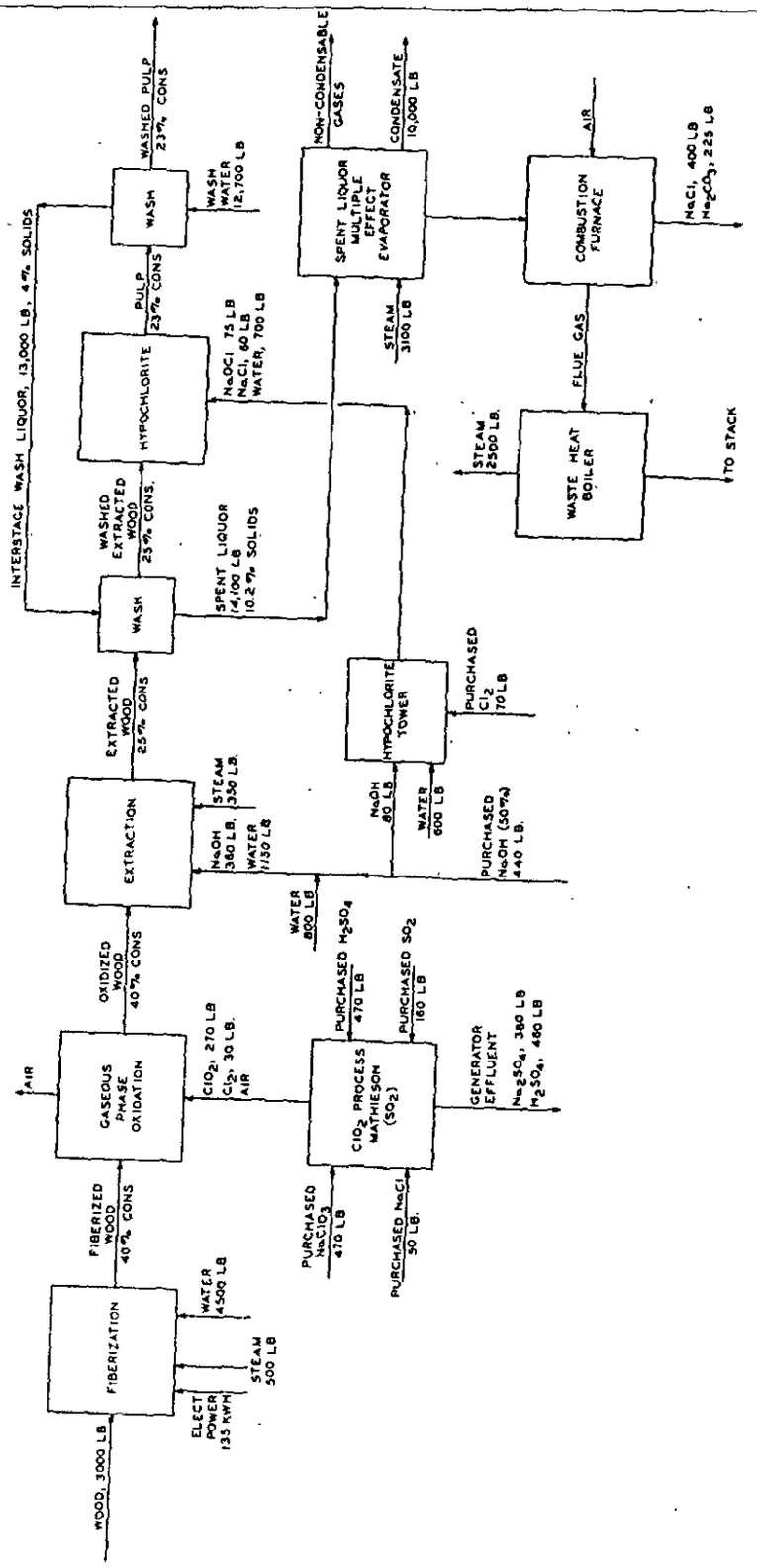


Figure 14. Flow Diagram with Incomplete Recovery

It would seem evident that the data shown in Fig. 14 reflect unfavorably on holopulping with incomplete recovery. There are two major reasons why such an approach does not appear promising. The first is the large amounts of chemicals which would have to be purchased, such as $NaClO_3$, NaOH, H_2SO_4, etc. The second is the large amounts of waste chemicals produced which must be utilized or disposed of. A summary of these chemical requirements and effluent loads for one ton of pulp is given in Table XIV. It may be noted that the generator effluent has a sulfur equivalent of 1050 lb. Na_2SO_4 per ton of holopulp. Assuming a kraft salt cake make-up rate of about 100 lb. salt cake per ton of kraft pulp, the operating ratio between kraft production and holopulp production would be about 10 to 1 if the kraft recovery system was to handle the effluent from the ClO_2 generator. Clearly, operating a holopulp process without complete recovery as an adjunct to a kraft process has limited applicability.

In summary, operation of a holopulp process without chemical regeneration entails large process chemical requirements and presents severe problems in disposal of waste chemicals. For these reasons, such an operation does not appear to be very practical. It would appear proper to devote major attention to the complete self-contained process.

TABLE XIV

SUMMARY OF CHEMICAL REQUIREMENTS AND WASTE CHEMICALS
FOR HOLOPULPING WITHOUT CHEMICAL REGENERATION

Chemical requirements,
lb./ton o.d. holopulp:

$NaClO_3$	470
NaCl	50
H_2SO_4	470
SO_2	160
NaOH	440
Cl_2	70

Waste chemicals,
lb./ton o.d. holopulp:

Na_2SO_4	380
H_2SO_4	460
NaCl	400
Na_2CO_3	225

ECONOMIC EVALUATION OF HOLOPULP

As the previous discussion has indicated, a complete closed-holopulping process appears to be technically within reach. This leaves the question of the economic feasibility of the process to be determined. Accordingly, an economic evaluation of the process is presented in the following. The cost estimates which are made should be considered as crude estimates since the process has not yet been developed to the point to warrant extremely detailed economic projections.

This economic analysis is divided into four areas: raw material costs, utilities costs, labor costs, and capital costs. It is felt that the most reliable estimates are for the first two categories, raw materials and utilities costs. The reason is that material and energy balance calculations have defined the requirements for raw materials and utilities. Multiplication by appropriate unit costs permits calculation of raw material and utility costs per ton of pulp. The greatest uncertainty would probably lie in the labor costs. Detailed engineering of the process has not proceeded to the point where labor requirements are definable. An estimate of labor needs can be made from information on various subloops in the process (e.g., chlor-alkali) and by analogy with existing processes. Capital costs are arbitrarily based on a production rate of 500 tons of o.d. pulp per day. Capital estimations are based on major units and blocks in the system since a detailed capital estimation for each item in the process is not warranted at present. All cost data are presented on the basis of one o.d. ton of holopulp. To convert to an airdry basis, all cost figures should be reduced by 10%.

RAW MATERIALS COSTS

Raw material requirements are dependent on whether the process includes chemical regeneration or not. In the complete system, the major raw material is

wood. There will also be a small amount of make-up chemical (primarily NaCl) and certain additive chemicals (e.g., barium carbonate and sodium dichromate). In addition, graphite for electrode replacement in chlor-alkali and chlorate cells and asbestos for diaphragm replacement can be considered as raw materials. In the case of holopulping with incomplete recovery, the major raw materials are wood and the chemical requirement. The chemical requirement is very high in this case, while raw material costs associated with the operation of chlor-alkali and chlorate cells are eliminated. Raw material cost estimates are presented in Table XV. These data are given for three process variations: complete holopulping with aqueous oxidation, complete holopulping with gaseous ClO_2-Cl_2 oxidation, and holopulping without chemical regeneration using gaseous oxidation. These variations are essentially those presented in Fig. 11, 13, and 14, respectively.

In the cases with a full recovery system, Cases I and II, the major raw material cost is the cost of wood. Wood costs could be highly variable depending on local conditions, and the values presented in Table XV should be taken as indicative only. The difference between the cost of red maple and aspen does appear to be real and significant. This difference is due mainly to red maple having a significantly higher basic density than aspen (0.49 as opposed to 0.35). Other raw material costs for Cases I and II are quite low, on the order of $3-4 per ton. Much of this is due to replacement costs for the graphite electrodes. These costs are presented as raw materials costs by estimating the lifetime of the electrodes and allocating this to the tonnages of Cl_2 and sodium chlorate, and hence to pulp production. This cost figure includes that portion of the graphite remaining when the electrodes are replaced. The cost of asbestos for diaphragm replacement appears to be negligibly small. This estimate is based on an asbestos consumption of 1.2 lb. per ton of Cl_2 obtained from the revised

edition of the Encyclopedia of Chemical Technology. Chemical costs as such are quite low for the cases with total chemical recovery systems. This may be contrasted with the costs for chemicals in Case III, where chemical regeneration is not practiced. Even with full credits given for by-products, the cost of chemicals alone is nearly $50.

TABLE XV

ESTIMATED RAW MATERIALS COSTS

A. Wood Costs

(Based on a requirement of 3000 lb. o.d. chips for one o.d. ton of pulp.)

(Calculations assume a 15% loss on barking and chipping.)

ASPEN COSTS: Assume $18.90 per rough cord delivered.

Assume 85 ft.^{3} solid wood per cord.

Basic density = 0.35.

Need: $\frac{3000 \text{ lb.}}{0.85} \times \frac{1 \text{ cord}}{0.35 \times 62.4 \times 85 \text{ lb.}} = 1.9$ cords/ton o.d. pulp.

Cost: 1.9 x $18.90 = $36. Aspen = $36 per ton pulp.

RED MAPLE COSTS: Assume $17.00 per rough cord delivered.

Assume 80 ft.^{3} solid wood per cord.

Basic density = 0.49.

Need: $\frac{3000 \text{ lb.}}{0.85} \times \frac{1 \text{ cord}}{0.49 \times 62.4 \times 80 \text{ lb.}} = 1.45$ cord/ton o.d. pulp.

Cost: 1.45 x $17 = $24.50. Red maple = $24.50 per ton pulp.

TABLE XV (Contd.)

ESTIMATED RAW MATERIALS COSTS

B. Other Raw Materials Costs

(All values per ton of o.d. pulp.)

CASE I: Complete Holopulping with Aqueous Oxidation (Fig. 11)

Make-up NaCl (assume 90% recovery):

70 lb. x 1¢/lb. = $0.70

Barium carbonate for sulfate purging:

4 lb. x 6.2¢/lb. = $0.25

Sodium dichromate to protect chlorate cell electrodes:

2.5 lb. x 15¢/lb. = $0.40

Graphite for chlorate cell electrodes:

3.25 lb. x 45¢/lb. = $1.50

Graphite for chlor-alkali cell electrodes:

1.6 lb. x 45¢/lb. = $0.72

Asbestos for diaphragm replacement:

0.25 lb. x 10¢/lb. = $0.03

Case I subtotal = $3.60

CASE II: Complete Holopulping with Gaseous Oxidation (Fig. 13)

Other raw material costs will be the same as for Case I, except that graphite for chlorate cell electrodes would be reduced by 17% to $1.25 to reflect the assumed drop in ClO_2 requirement from 9% to 7.5% on the wood.

Case II subtotal = $3.35

TABLE XV (Contd.)

ESTIMATED RAW MATERIALS COSTS

CASE III: Holopulping Without Chemical Regeneration (Fig. 14)

Cooking Chemical Requirements

Sodium chlorate:	470 lb. x 6.5¢/lb.	= $31.50
Sodium chloride:	50 lb. x 1¢/lb.	= $ 0.50
Sulfuric acid:	470 lb. x 1.4¢/lb.	= $ 6.60
Sulfur dioxide:	160 lb. x 3.5¢/lb.	= $ 5.60
Sodium hydroxide:	440 lb. x 3¢/lb.	= $13.20
Chlorine:	70 lb. x 3.5¢/lb.	= $ 2.45
	Case III chemical requirements total	= $59.85

Potential credits for effluents

Sodium sulfate (salt cake):	380 lb. x 1.4¢/lb.	= $ 5.30
Sulfuric acid:	460 lb. x 1.4¢/lb.	= $ 6.15
	Total credits	= $11.45
	Case III subtotal if maximum credits taken	= $48.40

TOTAL RAW MATERIALS COSTS

	Aspen	Red Maple
Case I	$39.60	$28.10
Case II	$39.35	$27.85
Case III	$84.40	$72.90
Case III (no credits)	$95.85	$84.35

Utilities Costs

The major costs for utilities will be for steam and electrical power. In addition, for aqueous oxidation systems, the water and recycled liquor to the ClO_2 absorber must be chilled. Three major, defined requirements for electrical power are the chlorate cells, the chlor-alkali cells, and the refiner used for the chip fiberization step. In addition, electrical power would be needed for the fan or compressor supplying air to the liquor combustion furnace as well as for pumps and other miscellaneous uses throughout the process. Steam is needed primarily for evaporation of the spent liquor, caustic evaporation, and chip fiberization. Steam is also used in the pulping steps for increasing temperatures to desired values. Utility cost estimates are presented in Fig. 16 for the three cases mentioned above. Power costs are taken at 5 mils/kw.-hr., and steam costs at 50¢/100 lb. The steam cost is based only on the steam deficiency, that is, the difference between the steam requirement and the steam generated by the waste heat boiler on the liquor combustion step.

The data in Table XVI clearly show the use of large amounts of electrical power in the complete holopulping process and the dependence of the process on the availability of cheap electrical power. Even with 5 mil power, electrical energy costs would run about $12 per ton of pulp. Steam costs can also be significant, particularly if care is not taken to maintain as high a spent liquor concentration as possible. The much lower utilities cost for Case III is a reflection of the trade-off in utilities costs and raw materials costs when regeneration of the cooking chemicals is eliminated.

TABLE XVI

ESTIMATED UTILITIES COSTS

Based on: 5 mils/kw.-hr. for electrical power
50¢/1000 lb. for steam
$1.50/$10^6$ B.t.u. for chilling water.
All values for one ton o.d. of holopulp.

CASE I. Complete Holopulping with Aqueous Oxidation (Fig. 11)

Electrical Power:

Chlorate cells	1300 kw.-hr.	
Chlor-alkali cells	580 kw.-hr.	
Fiberization	140 kw.-hr.	
Miscellaneous	400 kw.-hr.	
Total:	2420 kw.-hr.	= $12.10

Steam:

Spent liquor evaporation	5200 lb.	
Caustic evaporation	500 lb.	
Fiberization	500 lb.	
Oxidation step	900 lb.	
Extraction step	400 lb.	
Total required:	7500 lb.	
Less steam generated:	2500 lb.	
Steam deficiency:	5000 lb.	= $ 2.50

Chilling requirement:

Recycled liquor	1,100,000 B.t.u.	
Make-up water	250,000 B.t.u.	
Total:	1,350,000 B.t.u.	= $ 2.00

Case I Total Utilities Costs = $16.60

TABLE XVI (Contd.)

ESTIMATED UTILITIES COSTS

CASE II. Complete Holopulping with Gaseous Oxidation (Fig. 13)

Electrical Power:

Chlorate cells	1080 kw.-hr.	
Chlor-alkali cells	580 kw.-hr.	
Fiberization	140 kw.-hr.	
Miscellaneous	350 kw.-hr.	
Total:	2150 kw.-hr.	= $10.75

Steam:

Spent liquor evaporation	2900 lb.	
Caustic evaporation	500 lb.	
Fiberization	500 lb.	
Extraction step	400 lb.	
Total required	4300 lb.	
Less steam generated	2500 lb.	
Steam deficiency	1800 lb.	= $ 0.90

Case II Total Utilities Costs = $11.65

TABLE XVI (Contd.)

ESTIMATED UTILITIES COSTS

CASE III. Holopulping Without Chemical Regeneration (Fig. 14)

Electrical Power:

Fiberization	140 kw.-hr.		
Miscellaneous	260 kw.-hr.		
Total:	400 kw.-hr.	=	$ 2.00

Steam

Spent liquor evaporation	3100 lb.		
Fiberization	500 lb.		
Extraction	400 lb.		
Total required:	4000 lb.		
Less steam generated:	2500 lb.		
Steam deficiency:	1500 lb.	=	$0.75

Case III Total Utilities Costs = $ 2.75

LABOR COSTS

Estimation of labor costs at this stage of the process development is subject to a great deal of uncertainty. In general, it should be possible to minimize labor requirements since the process is essentially a continuous process and should be quite adaptable to extensive automatic control. The use of electrolytic chlorate and chlor-alkali cells will of course require a certain amount of labor for changing electrodes and diaphragms. Other labor requirements are less easily defined.

In order to make an estimate of the labor required, a daily pulp production rate of 500 tons of pulp will be assumed. It will also be assumed that the process is reasonably well monitored and automatically controlled. A 500-t.p.d. pulp production would require 100 tons/day chlorine production and about 70 tons/day ClO_2. The Encyclopedia of Chemical Technology gives the cell-room maintenance labor requirement for diaphragm cells as 0.29 man-hr./ton Cl_2. This would be equivalent to 29 man-hr. in this case, or about 4 man-days. It is assumed that the equivalent in maintenance for the ClO_2 system would also be required. It is further assumed that 4 operators per shift would be required for the combined chlor-alkali and ClO_2 systems. Essentially one each for chlorate cells, ClO_2 generator, chlor-alkali cells, and caustic evaporator. For the evaporation and combustion of spent liquor, it is assumed that 3 men per shift would be used as operators plus 3 man-days for maintenance. For the pulping step, 3 men per shift are assumed as operators plus 5 man-days for maintenance. These estimates total out at 46 man-days or 368 man-hr. for 500 tons of pulp. Thus the estimated labor requirement is 0.74 man hr. per ton of pulp. As a safety factor, this may be raised to 1 man-hr./ton, in which case supervisory labor would also be included. If a value of $7.50 per man-hr. is

attached to labor, the estimated labor cost becomes $7.50 per ton of pulp. If the system of holopulping without chemical regeneration is used, this might be reduced to about $5.00 per ton of pulp at the same capacity. A summary of these estimates is presented in Table XVII.

TABLE XVII

ESTIMATED LABOR COSTS

(Based on production of 500 tons of pulp per day)

Chlor-alkali cell room maintenance:	4 men
Chlorate cell and ClO_2 maintenance:	4 men
Combined ClO_2 and chlor-alkali operation (4 men/shift):	12 men
Evaporation and combustion operation (3 men/shift):	9 men
Evaporation and combustion maintenance:	3 men
Pulping operation (3 men/shift):	9 men
Pulping maintenance:	5 men
Total:	46 men

Total man-hr./day = 46 x 8 = 368 man-hr.

Man-hr./ton = 368/500 = 0.74 man-hr./ton.

Hence, Labor requirement = 1 man-hr./ton is assumed to be reasonable.

Labor cost = 1 man-hr./ton x $7.50/man-hr. = $7.50.

CAPITAL COSTS

The estimation of capital requirements is based on an assumed production of 500 tons of o.d. pulp per day. Capital costs are in general based on large blocks of equipment and major units and not on details. Capital estimates are presented in Table XVIII for the same three cases discussed previously. The means of arriving at these figures is discussed below.

The capital cost of the ClO_2 system is based on an estimate by Chemech for an integrated chlorate/ClO_2 plant of 50 tons of ClO_2 per day production capacity They estimate $7,500,000 for the integrated plant of which $5,500,000 is for the chlorate plant and 2,000,000 is for the ClO_2 plant. This is an estimated cost for battery plants on prepared site with all services provided to battery limits and includes royalties. The 0.6 power rule was used to project this cost to other production rates. There is some reason to believe that this estimate may be somewhat on the high side.

The cost of the chlor-alkali system was determined from three independent sources for grass-roots electrolytic chlorine plants, namely, the Encyclopedia of Chemical Technology, the book, "Strategy of Process Engineering" by Rudd and Watson, and an article on the chlor-alkali industry in the March, 1965, issue of Chemical Engineering Progress. All three methods predict a capital cost of about $8,000,000 for a 100-ton-per-day chlorine production rate. This figure would tend to be somewhat high since all parts of a merchant chlorine plant would not be required in the holopulp system. On the other hand, the data in these published sources are about 5 to 10 years old and would not account for inflation. Because these effects would tend to balance each other, the figure of $8,000,000 for 100 tons of Cl_2 per day was used.

TABLE XVIII

ESTIMATED CAPITAL REQUIREMENTS

(Based on 500 tons o.d. pulp/day production. All values as millions of dollars.)

	Case I (Fig. 11)	Case II (Fig. 13)	Case III (Fig. 14)
Pulping Step:			
Wood preparation	2.5	2.5	2.5
Fiberization	0.5	0.5	0.5
Reactors	3.0	3.0	3.0
Washing	1.5	1.5	1.5
Spent Liquor Processing:			
Evaporators	1.6	1.05	1.1
Combustion Furnace	1.0	1.0	1.0
Waste Heat Boiler	0.1	0.1	0.1
Chlorine Dioxide System:			
Chlorate	6.75	5.9	-
ClO_2 generation	2.45	1.65	2.3
Chlor-Alkali System:	8.0	8.0	-
Chemical Handling:	-	-	1.0
Totals:	27.4	25.2	13.0

The capital cost estimate for the spent liquor processing is based on separate estimations for multiple-effect evaporators, the furnace, and the waste heat boiler. Evaporator costs are based on 4 effects with an assumed driving force of 25°F. and an overall coefficient of 400 B.t.u./hr. ft.^{2} °F. A table giving installed costs of LTV evaporators as a function of total area in the fourth edition of Perry's "Chemical Engineer's Handbook" was used. This was adjusted by a factor of 1.8 to account for price differences between 1960 and 1970 and for the possible use of materials other than steel. This gave an evaporator cost of $1,250,000 for an evaporation requirement of 12,000 lb. water per ton of pulp. A scale factor of 0.7 was used to calculate costs at other evaporation loads. The waste heat boiler was conservatively estimated at $100,000 based on a load of 50,000 lb./hr. low-pressure steam. Data from Rudd and Watson's book, "Strategy of Process Engineering," was used. The capital cost for a fluidized-bed combustion furnace was arbitrarily set at $1,000,000 for lack of better information. This value is the same as the cost for a process furnace at the same heat release rate of 180,000,000 B.t.u./hr. according to an article by Guthrie in the March 24, 1969, Chemical Engineering magazine.

Capital cost estimates for the pulping step itself are based on estimates for specific units, namely, wood preparation, fiberization, oxidation, extraction, hypochlorite, and washing. Wood preparation was assumed to cost $2,500,000. Refiners for fiberizing are estimated at $500,000. Each stage of the pulping step was assumed to cost $1,000,000, with $1,500,000 allocated for pulp washing. The same reactor cost was assumed for both gaseous and aqueous oxidations. It was felt that the increase in size due to lower bulk density and the materials handling problems with the gaseous reactor would be counterbalanced by shorter reaction times, less internal pressure, and the elimination of liquor recycling and pulp dewatering.

TOTAL COST

An estimate of the total cost per ton of pulp can be obtained by adding together the raw material, utility, and labor costs together with a proration of the capital cost to a tonnage basis. In order to allocate capital costs onto a tonnage basis, straight-line depreciation of 10% is assumed plus an interest charge of 8%. A total of 350 operating days per year is assumed. Total cost estimates per ton of o.d. pulp for both aspen and red maple are given in Table XIX.

Bearing in mind that the data on which these total cost estimates were made is somewhat uncertain, the cost outlook for holopulp appears promising. Taking the more favorable case, Case II, it appears that holopulp can be made (in slush form) for about $85/ton with aspen and about $75/ton with red maple. On the basis of an air-dried ton of pulp, these costs become about $77/ton and $67/ton, respectively. It would appear that costwise, holopulp can be competitive with bleached kraft under the proper circumstances, namely, with cheap electrical power available. In comparing holopulp with bleached kraft, holopulp requires a significantly higher utilities cost due to the electrolytic regeneration of chemicals which is counterbalanced by savings in wood costs due to the substantially higher yield.

It would appear that the stage of making crude cost analyses to permit cost comparisons with kraft has reached a point of diminishing returns. On the basis of these analyses, the costs are comparable. Further development work on the holopulp process is now required to solve the remaining technical problems and to allow for a more detailed and accurate cost projection.

TABLE XIX

ESTIMATED TOTAL COSTS PER O.D. TON OF HOLOPULP

	Case I	Case II	Case III
Aspen			
Raw materials	$39.60	$39.35	$84.40
Utilities	$16.60	$11.65	$ 2.75
Labor	$ 7.50	$ 7.50	$ 5.00
Capital charges	$28.20	$25.90	$13.40
Total:	$91.90	$84.40	$105.55 (with full credits)
Red Maple			
Raw materials	$28.10	$27.85	$72.90
Utilities	$16.60	$11.65	$ 2.75
Labor	$ 7.50	$ 7.50	$ 5.00
Capital charges	$28.20	$25.90	$13.40
Total:	$80.40	$72.90	$94.05

DISCUSSION OF PROBLEM AREAS

The preceding discussion has been concerned with the various elements of holopulping, their synthesis into a self-contained process, and the economic outlook for this process. In this discussion, various technical problem areas were alluded to and considered. It seems pertinent to reconsider these areas of the process where uncertainty exists in order to provide a focus for further development work.

SPENT LIQUOR PROCESSING

The biggest single unknown in the process as it presently stands lies in evaporation and combustion of the spent liquors. Minimal laboratory work has been done on this aspect of the process, and it is not possible to borrow directly from existing technology since these particular liquors have not previously existed. Certain key questions must be answered before the technical success of the process as presently constituted can be relied upon.

Evaporation

A good deal of information is required on evaporation of the spent liquor. Probably most important is the determination of whether or not potential pollution problems are associated with the evaporation step. Specifically, this would involve the possible presence of volatile chlorine compounds in the noncondensable gases which could cause air pollution and the presence of chlorine compounds or low-boiling organics in the condensate which could cause stream problems. It will be necessary to determine the extent to which these problems exist and the possibilities for alleviating them through changes in pulping conditions and the sodium-chlorine ratio in the spent liquor. Evaporation condensates must be characterized to fully evaluate the potential for condensate reuse in the process.

In addition to the possible pollution problems in evaporation, certain data related to operating characteristics must be obtained. The viscosity of the spent liquor as a function of temperature, solids concentration, and inorganic-organic ratio should be determined. Any tendency toward solids precipitation as evaporation proceeds should be uncovered. An investigation of the foaming or scaling tendencies of these liquors should be made. Finally, some measure of the corrosiveness of holopulp spent liquors would be needed in order to properly select materials for the evaporator.

Combustion

At present, liquor combustion appears to be the key step in the recovery process. The entire regeneration system is predicated on the ability to obtain all sodium and chlorine as sodium chloride and sodium carbonate after combustion of the liquor. Although these products were obtained in some preliminary work on burning combined spent liquors in a muffle furnace, those results were not sufficiently quantitative or general to permit the assumption that they will, in fact, be the predominant products in commercial combustion. This must be reliably established.

There are several aspects to the combustion problem which are interrelated. The first is the chemical composition of the solid (or molten) products leaving the furnace. Are they, in fact, NaCl and Na_2CO_3? The second question is with regard to the composition of the flue gases leaving the furnace. Are there any chlorine compounds present which would cause air pollution problems? Finally, there is the question of the amount of solids present in the combustion gases. The relatively high volatility of sodium chloride makes this a real possibility. Would an electrostatic precipitator be required?

One of the major requirements is to determine the proper temperature range for carrying out the combustion, and, from this, to determine the type of furnace to be used. Several factors are involved here. The volatility of sodium chloride and the melting point of the sodium chloride-sodium carbonate mixture could exert a significant restraint on furnace temperature. The effect of temperature on equilibria and hence on the composition of the furnace products must be considered. The optimum temperature would be that which maximized the formation of NaCl and Na_2CO_3 and minimized the formation of gaseous chlorine compounds. Finally, the ability to maintain stable combustion, while evaporating the remaining water from the liquor, could be affected by the operating temperature and would have to be considered.

There would appear to be advantages in carrying out the combustion at temperatures below the melting points of sodium chloride and sodium carbonate using fluidized-bed techniques. There are two requirements to be met for this approach to succeed. First, the desired furnace products, NaCl, Na_2CO_3, CO_2, and H_2O, would have to be obtained at relatively low temperatures. Secondly, the solid particles formed during combustion would have to have the proper characteristics to support a fluidized bed. This possibility should be investigated.

It will be necessary to determine the heating values of the holopulp spent liquors as functions of solids content and organic-inorganic ratio. This would permit a determination of the need for auxiliary fuel as well as the degree of concentration needed in the evaporators. It would appear to be critical to avoid the introduction of sulfur into the system through the use of auxiliary fuel.

WATER BALANCE

The second biggest problem in the holopulping process concerns the water balance over the pulping steps and the resulting dilution of the spent liquor. Each step in the pulping operation has the potential for adding water to the system and must be carefully controlled to avoid dilution of liquors. This problem is accentuated by the relatively large number of individual operations in holopulping. Oxidation, extraction, hypochlorite, and washing steps must all be carried out in such a fashion as to minimize the addition of water to the system. In essence, this requires either direct operation at high consistency (preferably above 20%) or internal recycle of the liquors. The need to keep water addition to a minimum can have significant effects on the type of equipment to be used in pulping and could affect the pulping reactions themselves.

Recycling of Liquors

One method of minimizing water addition in the pulping steps is to dewater the stock leaving the reactors and recycling the liquor back into the reactor. This step is mandatory with aqueous-phase oxidations, since the low solubility of ClO_2 in water requires a very large amount of water entering the reactor to carry the ClO_2. This method could also be used for the extraction and hypochlorite steps. In the latter cases, the consistency in the reactors would be governed by mixing and uniformity considerations rather than by chemical solubilities.

One of the important factors governing liquor recycling is the ability to dewater the stock leaving a given reactor. The amount of liquor available for recycle will depend on the consistencies before and after dewatering. Under some circumstances, the dewatering capability will control the water balance on a given unit. If the extent of dewatering is limited, more water will leave with the pulp

and additional water would be added to the recirculating liquor to maintain a water balance. This would undoubtedly be the case with aqueous oxidations. However, dewatering capability would not always control the water balance. The water leaving a given step with the stock must equal the water entering the step with the stock, with cooking chemicals, or as steam. Dewatering beyond this limit point (even if mechanically feasible) would only result in an accumulation of water within the unit which would eventually have to be discharged to the spent liquor. In order to evaluate the possibilities for water balance control it is necessary to have data on the extent to which holopulps can be dewatered at each stage of the pulping process. These data would have to be such that the extent of dewatering on commercial equipment could be predicted. The range of interest would be consistencies between 20 and 30%.

Another factor involved with recycle of liquors is the effect on the pulping reactions. This problem has two aspects. The first is the possibility that active chemical would be consumed by recycled material. This would increase the amount of chemicals needed to carry out a given operation. This problem would probably be most severe with aqueous-phase oxidations, since the goal in that step is to use the minimum amount of a highly reactive chemical. It could also be present in extraction and hypochlorite treatment. The second aspect concerns interference with the pulping reactions other than by competing for active chemical. For example, it would be undesirable for recycled materials to reprecipitate on the fibers. Experimental data on the effects of recycling liquors on each of the pulping steps are needed to properly evaluate the recycle approach to water balance control.

High-Consistency Reactors

An alternative approach to water balance control is carrying out each of the pulping steps at high consistency (greater than 20%). This approach is, of course, impossible with aqueous oxidations because of the limited solubility of ClO_2. However, gaseous oxidations do permit high-consistency operation. The problems of gaseous oxidations will be discussed later in this section. Concern for the present is directed at the possibility of carrying out the extraction and hypochlorite stages at high consistency. This would appear to be essentially a problem in mixing the chemicals and stock entering the reactors. Both the extraction and hypochlorite steps use aqueous solutions of active chemicals. If these can be uniformly applied to the fiber and fiber bundles at high consistency, the remainder of the reaction should be straightforward. The problem lies in the fact that the consistency range is such that little, if any, free water is available (short of mechanical pressing). This might make it necessary to spray the active chemical onto the stock in a uniform manner. An alternative approach would involve setting up a dewatering and recycle loop over the mixing step itself. Mixing could be carried out at a lower consistency and then the material would be dewatered. The expressed liquor would be mixed with the concentrated chemical stream and used to dilute the pulp entering the mixer. This would permit high-consistency operation in the reactor itself. At the current stage of the holo-pulping process, it does not appear to be necessary to become involved in the development of high-consistency reactors. However, exploratory work on the effect of high consistency on the pulping reactions should be carried out. In addition, the availability of commercial equipment to carry out high-consistency reactions should be explored.

Washing

Washing plays an exceedingly important role in the water balance problem. Not only must washing be carried out at low dilution factors, but it must be compatible with the rest of the pulping operation, namely, it must be carried out effectively at high consistency.

The first factor of importance regarding washing is to determine where washing is needed. Obviously, washing must be carried out on the pulp leaving the last stage of the pulping process (nominally the hypochlorite stage). However, since the pulping process consists of a sequence of distinct operations, the possibility exists that washing may be needed between stages. This would be determined primarily by the effect of residual materials (those not washed out) on subsequent processing steps. In this respect, the problem is similar to the problem of interference with reactions when recycling liquors within a given step. The important difference would be that the reaction products which might interfere would derive from previous steps. In considering the need for interstage washing, it must be recalled that the bulk of the material is solubilized in the extraction step. Thus, it would appear likely that washing between the extraction and hypochlorite steps would be more important than washing between the oxidation and extraction steps. This must be determined. Interstage washing requirements are very important because they determine the washing configuration to be used. The strongest argument against multistage pulping, for example O-E-O-E-H, is the likelihood that a fresh water wash would be needed between the first extraction and second oxidation. Hence, the interstage washing requirements must be defined, and the effects of omitting washing on subsequent pulping steps determined.

The second factor of importance in washing is the ability to get effective washing with minimum water use at high consistency. It does not appear that this would require the development of new washing methods but rather the selection from among available techniques those which are most appropriate for this requirement. In general, it would appear that drum washers would not be suitable for holopulp washing because the consistency on the drum would be too low. High-consistency diffusion washing would seem to be a promising approach. Press washing could also be used. It is likely that a proper combination of diffusion washing and dewatering presses would be satisfactory. There is a need for a comprehensive survey of equipment available for carrying out high-consistency washing (preferably above 20% consistency). This information could then be used to configure a washing system suitable for holopulp.

Water Balance Summary

The water balance in the pulping steps is a critical problem. It is not dependent on any given step but is controlled by all steps in the pulping operation. Strict control of water addition must be maintained over all steps, oxidation, extraction, hypochlorite, and washing. There is great incentive to minimize fresh water interstage washing. In general, the water balance problem can be met by recycling liquors at the various pulping steps, carrying out the reactions at high consistency whenever possible, and by judicious use of high-consistency washing techniques. Appropriate combinations of these methods can be used, such as the use of recycle with an aqueous oxidation and high-consistency operation in the extractor.

GASEOUS-PHASE OXIDATIONS

As has been pointed out in the previous section of this report, there are pronounced process advantages if the oxidation can be carried out by reacting the ClO_2 generator gases directly with moist fiberized wood. This would involve the use of a gas containing about 1/2 mole of Cl_2 for each mole of ClO_2. The major question is whether the use of chlorine gas in such proportions would result in intolerable degradation of ultimate pulp properties. This must be determined. The potential advantages of the direct gaseous approach are sufficiently great to warrant the effort. This could be answered through laboratory investigations which would have two essential goals: evaluation of the effect on pulp properties of increasing amounts of chlorine in a gaseous ClO_2-Cl_2 oxidation step spanning the 1/2 mole Cl_2-1 mole ClO_2 concentration range, and determination of the effect of chlorine addition on the total ClO_2 requirement since a decrease would have significant economic benefit.

In the event that laboratory studies such as those mentioned above proved successful and it was demonstrated that Cl_2-ClO_2 mixtures of the right proportions could be used, it would be necessary to initiate work on the development of a reactor for carrying out a gaseous oxidation. Problems which would have to be solved would include means for feeding the fiberized wood into the reactor, means for maintaining uniform contact of reactive gases and fiberized wood within the reactor while maintaining reasonable bulk densities of the material, means for providing for fiberized wood transport through the reactor, and discharge methods which would not involve an air emissions problem with unreacted gases. It does not appear worthwhile to be concerned with the gaseous reactor design until it has been demonstrated that 1/2 Cl_2-ClO_2 gas mixtures are suitable. However, if the reaction is favorable, development of an appropriate reactor would be important.

CHLORINE DIOXIDE SYSTEM

Most of the uncertainty in the ClO_2 system is due to lack of knowledge of details of the process and can be resolved through discussions with Chemech. One problem is with regard to the use of hydrogen gas as a diluent for the gases leaving the generator, as was inferred from the Chemech patent. It is not known whether this method is actually used by Chemech. It is quite possible to set the system up to use air or nitrogen as the carrier gas. A problem in inventory control could be present with the closed gas cycle in the Chemech process. This problem is avoided if direct gaseous oxidation can be used in pulping. A major uncertainty lies in the roles played by gaseous hydrogen chloride and aqueous hydrochloric acid in the generator. A clarification on this point is important as it will determine whether or not it is necessary to provide for chlorine storages in the chlor-alkali system. The tolerance of the Chemech system for water addition must be determined since this could affect the need to dry the hydrogen and chlorine from the diaphragm cells. A potential problem of contamination of the ClO_2 system with organic compounds exists if aqueous oxidations are used, since recycled liquor would be sent to the ClO_2 absorber. This problem must be evaluated. In general, there do not appear to be critical problems in ClO_2 generations. The Chemech ClO_2 process has been successfully piloted and the Chemech chlorate cell has met with commercial success. Although the entire system has not yet been used commercially, there are good nontechnical reasons for this, and it should not be taken as a reflection on the technical soundness of the approach.

MISCELLANEOUS PROBLEMS

There are many areas where problems might exist or where information is lacking. There is a need for further data on steam and power requirements for

fiberization as well as the effect of fiberizing conditions on subsequent processing and pulp properties. Kinetic data are needed on the various pulping steps, particularly oxidations, in order to properly size reactors. It would be advisable to determine if the presence of NaCl in the caustic has any effect on the alkaline extraction since this could exert a constraint on the caustic evaporation requirement.

Another potential problem is whether or not the brine purification system would be effective. There are no obvious reasons why it should not, particularly if the furnace reactions come out as expected. However, electrolytic cell systems can be quite sensitive to impurities, so that a potential problem is present.

Finally, there is the general problem of corrosion in this system. Chlorine dioxide, chlorine, hypochlorite, hydrogen chloride, and caustic soda are the chemicals involved in this process. Corrosion problems can exist at practically all parts of the process. This will have a pronounced effect on the selection of materials for various process components.

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